

## Structure, Formation, and Decomposition of APB's in Calcic Plagioclase

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**Abstract.** In calcic plagioclase (Ca, Na) [(Al, Si) AlSi<sub>2</sub>O<sub>8</sub>] Al–Si ordering produces superstructures with periodic and non periodic antiphase boundaries (APB's). Crystals growing at high temperature close to the melting point and cooling fairly rapidly order by nucleation of ordered domains which grow, resulting in an irregular pattern of curved APB's (*b* plagioclase). A modulated structure with periodic APB's forms by continuous ordering at large undercooling below the critical ordering temperature (*e* plagioclase). During annealing APB's are eliminated by pairwise recombination of adjacent APB's to reduce strain energy along the boundaries thereby transforming nonstable *e* plagioclase into stable *b* plagioclase without change in chemical composition. This process is often accompanied by a chemical phase separation with APB's providing favorable surfaces for diffusion. Transformations are documented by *transmission electron microscopy* (TEM) micrographs illustrating the variation in morphology of APB patterns in igneous and metamorphic plagioclase. They are in agreement with Korekawa et al.'s (1978) model of intermediate plagioclase which relies on periodic stacking of basic units rather than wavelike modulations. The paper includes observations of a new type of satellite in Stillwater bytownite ('h' satellites) which are due to fine lamellar exsolution.

### Introduction

Minerals belonging to the plagioclase solid solution series are the most common constituents of the earth's crust. Two substitutions, Al–Si coupled with Ca–Na, allow for both exsolution and ordering. Diffusion is slow and difficult to achieve in the laboratory. An interpretation of subsolidus phase relations has therefore to rely largely on comparative studies of geological samples which formed under a variety of conditions ranging from rapid cooling from high temperatures within a few seconds in volcanic rocks to crystallization at medium temperatures and annealing for millions of years in metamorphic rocks. Grove (1977) and

Nord et al. (1974) have recognized different morphologies of antiphase domains in calcic plagioclase and related them to the thermal history. With new observations based on a large number of specimens we are getting more confidence about the range of representative microstructures which allows us to come up with a comprehensive model and structural interpretation about formation and decomposition of the periodic antiphase structure of *e* plagioclase.

Several models have been proposed for the structure of *e* plagioclase, most recently discussed and compared by Morimoto (1979). We feel that only one model – that by Korekawa et al. (1978) has survived the scrutiny of a rigorous and quantitative structure refinement and we use it as the basis for our discussion.

The most important part of the plagioclase structure is an Al–Si tetrahedral framework with Ca and Na occupying large interstices. The framework can be described by chains consisting of four-membered rings of tetrahedra which extend parallel to *z* and are linked three dimensionally. At low temperatures the Al–Si distribution is ordered to avoid Al–O–Al bonds. In the basic triclinic structure of albite (Fig. 1a) there are four non-equivalent tetrahedral sites over which Al and Si are distributed. In the Ca-rich end-member anorthite with an Al/Si ratio of 1, order can only be achieved if the unit cell is doubled along *z* (Fig. 1c) and *b*-superstructure reflections ( $h+k$  odd,  $l$  odd) are observed in the diffraction pattern. In this structure there are eight nonequivalent tetrahedral sites. Nonstoichiometric intermediate compositions (e.g., An 65) show a variety of superstructures. They can be viewed in a first approximation as different stacking arrangements of the units “A” and “B” in Fig. 1b. X-ray

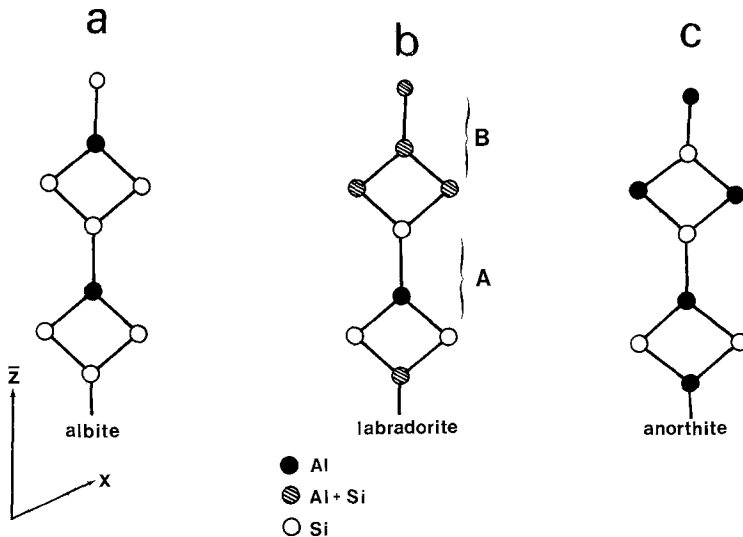


Fig. 1a–c. Schematic sketch illustrating the Al/Si distribution in the tetrahedral framework of plagioclase. Each circle represents an Al or Si atom. Oxygens are omitted. a Albite. b Labradorite An 66 (“*b*” plagioclase from Lake County, c.f., Tagai et al. 1980). Units A and B are indicated. c Anorthite

structure refinements of labradorite show that in some crystals A and B alternate regularly producing a 14 A  $\bar{1}\bar{1}$  structure of "b-plagioclase" with sharp *b*-reflections in the diffraction pattern (Tagai et al. 1980). The lattice geometry is similar to that in anorthite (Fig. 1c) but the Al-Si distribution and the chemical composition is different. In other crystals of labradorite the regular stacking is interrupted by periodic antiphase boundaries (APB's) giving *e* plagioclase, characterized by incommensurate *e*-satellites instead of *b*-reflections in the diffraction pattern (Korekawa et al. 1978). In some rapidly quenched volcanic labradorite there is only short range order with highly diffuse and weak superstructure reflections (Wenk et al. 1980). Notice that the structural unit A [consisting of tetrahedra  $T_1(\text{Oz})$ ,  $T_1(\text{mz})$ ,  $T_2(\text{mO})$ ,  $T_2(\text{Oz})$ ] stays constant over the whole composition range of the plagioclase solid solution. The unit B ( $T_1(\text{OO})$ ,  $T_1(\text{mO})$ ,  $T_2(\text{OO})$ ,  $T_2(\text{mz})$ ) changes in composition from  $\text{AlSi}_3$  to  $\text{Al}_3\text{Si}$  and also changes the ordering pattern. In spacegroup  $\bar{1}\bar{1}$  this unit appears partially disordered in intermediate compositions but it is likely that this is due to superposition and unit B could be decomposed in a spacegroup of lower symmetry into ordered units. In most intermediate plagioclase diffuse *c*-reflections ( $h+k$  even,  $l$  odd) are present which indicate short range order of some sort in  $\bar{1}\bar{1}$  symmetry.

### Samples and Methods of Analysis

Geological history, composition and microstructural observations of the specimens studied are summarized in Table 1. Some samples have been described in other papers and reference is made to that work. An contents range from An 45 to An 75 except for an unusual albite-anorthite intergrowth. They were determined by electron microprobe, Universal stage petrographic microscope and energy dispersive X-ray analysis in the transmission electron microscope (TEM). Crystals for the electron microscope study were removed from petrographic thin sections and thinned to electron transparency by ion-beam etching. These foils were then analyzed with a JEM 100C TEM instrument equipped with a side entry tilt-rotation stage by standard techniques of brightfield and darkfield imaging, and selected area diffraction, making extensive use of the X-ray analytical capabilities. No *scanning transmission electron microscopy* (STEM) attachment was available and the minimum beam size was therefore around 200 nm (=2,000 Å) in diameter. Crystallographic orientation of the photomicrographs and operating beams are displayed in inserted diffraction patterns. In most cases diffraction patterns are slightly tilted into a symmetrical setting. Darkfield photographs have been obtained with strong *e* and *b* reflections.

### Observations and Interpretation

#### *Periodic APB Structure in Intermediate Plagioclase*

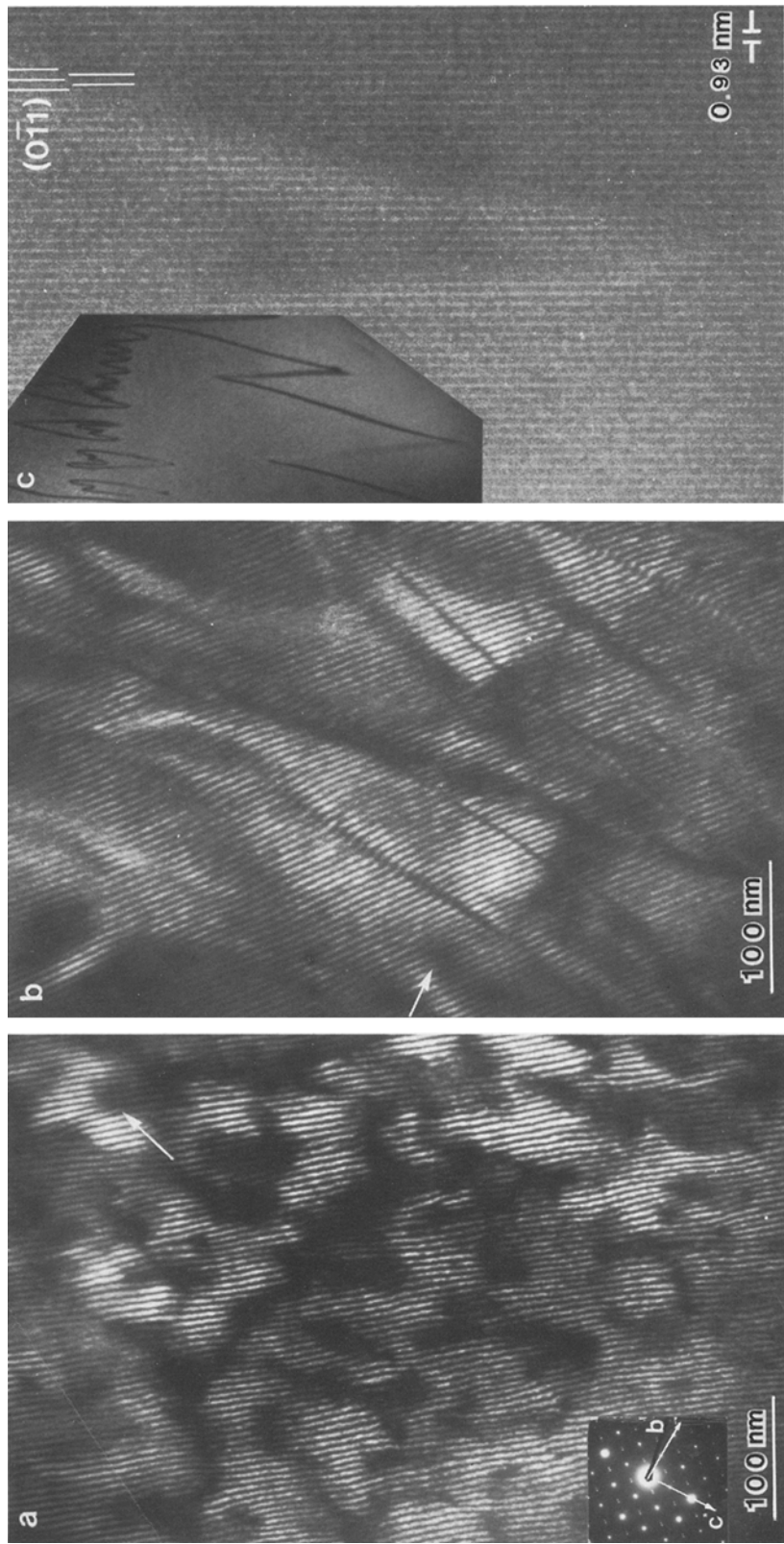
Labradorites and bytownites in metamorphic and many plutonic rocks show an incommensurate superstructure with satellites in the diffraction pattern.

**Table 1.** List of plagioclase samples used in this study

Sample #	An	Occurrence	Description of microstructure	$T$ (Å)	References
<i>Rapidly cooled volcanic rocks forming at temperatures between 1,000° and 1,300° C</i>					
Ss1	63	Air quenched phenocrysts. Eruption of Surtsey, Iceland	Diffuse $e$ . No microstructure can be resolved	30	Figs. 2a in H.R. Wenk et al. (1980)
LC1	66	Massive basalt flows. Plush, Oreg.	Sharp $b$ , diffuse $e$ . Curved $b$ APB's, spaced 300–500 Å		Stewart et al. (1966) Figs. 2b, 9 in H.R. Wenk et al. (1980)
Col 13	60–70	Phenocryst in andesite, Volcano Colima, Mexico	$b$ APB's, spaced 1,000–2,000 Å. Local regions with sharp $e$		Tagai et al. (1980)
<i>Anorthosites and layered intrusions. Medium cooling rates</i>					
SW-8	78	Stillwater, Mo., upper anorthosite zone	Large zig-zag $b$ APB's with secondary fine exsolution. Locally two types of satellites ( $e$ and $h$ )	60	Nord et al. (1974) Figs. 2c, 7b, c
SW-5	72	Stillwater, chromite zone	Similar to SW-8		Fig. 7a
SK 475	66	Skaergaard	Regular $e$ APB interrupted by curved boundaries	60	
984-109	70–80	Associated with granulites of the Musgrave block (S. Australia)	Local relicts of $e$ APB's, mostly zig-zag boundaries		Fig. 6e
N1	35+65	Schiller labradorite from Nain	Lamellar structure with periodic APB's in both parts	45+60	e.g., Hashimoto et al. (1976) Fig. 7d
Sb1	50	Sudbury	Very regular primary periodic APB's interrupted by curved APB's	60	E. Wenk (1979) Fig. 2a
JN03	70–80 ( $e$ : 70, $b$ : 75–80)	Japan, gabbro	Periodic $e$ structure with II wedges.	50	Figs. 4b, 6d, f
SLu 7	75	Deformed anorthosite along San Andreas fault. San Bautista, Calif.	Beginning segregation by recombination with formation of wedges.	60	Fig. 6a, b
<i>Metamorphic rocks. Slow cooling rates</i>					
Vz 433	64	Calcsilicate rock, amphibolite facies. Gordemo, Central Alps	Regular periodic APB pattern interrupted by curved boundaries.	30–40	E. Wenk et al. (1975); Fig. 2c in H.R. Wenk et al. (1980)

Sample #	An	Occurrence	Description of microstructure	$T$ (Å)	References
<i>Metamorphic rocks (continued)</i>					
PK 834	40	Andesine vein in amphibolite. Centovalli, Alps.	Same as above.	30	
Sci 1649	40 (plus 0 and 95)	Actinolite-pargasite schist. Amphibolite facies, Cavloccio, Bergell Alps	Regular $e$ APB structure in andesine decomposing by recombination into $P\bar{1}$ anorthite and albite	(35) to 50 to 65	Fig. 5 in H.R. Wenk (1979b). Fig. 4c
Sci 1583	45 (plus 0 and 95)	Same as Sci 1649	Similar to Sci 1649 but with zig-zag APB's in some regions	60	Fig. 2b
Vz 746	65 (plus 33 and 92)	Calclitic rock near migmatites. V. Carecchio, Central Alps	Regular $e$ fringe pattern decomposing by recombination into $b$ plagioclase	60	E. Wenk and H.R. Wenk (1977); Fig. 8 in H.R. Wenk (1978) Fig. 4a, d
Sci 974	67	Contact of amphibolite with tonalite	Relict periodic structure in a few areas. Mostly zig-zag $b$ APB's	70	Fig. 2d in H.R. Wenk et al. (1980)
Spl 43f	$e$ 65-70 $b$ 75-85	Calcareous schist, amphibolite facies. A. Dorca, V. Antigorio, Alps	Periodic structure decomposes into wide lamellae. Ca-rich lamellae have widely spaced APB's	70	Figs. 4e-i, 6c

McConnell and Fleet (1963) were the first to image a fringe structure with the electron microscope in darkfield with  $e$  reflections operating. The fringes have similar contrast as  $b$  APB's and are interpreted as periodic antiphase boundaries with a displacement vector  $\mathbf{R} = \frac{1}{2}[\mathbf{c}]$ . In order to see them clearly APB's have to be exactly edge-on. This requires that the irrational modulation vector  $\mathbf{T}$  (or the satellite vector  $\mathbf{t}$  where  $\mathbf{T} = \frac{1}{\mathbf{t}}$  which connects two  $e$  satellites;  $\mathbf{T}$  is the spacing between two  $e$  fringes in micrographs) has to be rotated into a position normal to the electron beam. Furthermore the crystal has to be tilted around this vector until some low order index Laue zone which contains strong satellites is in reflecting condition. This is often difficult or impossible to accomplish. But even if  $e$ -fringes are not resolved a domain structure can be imaged in darkfield which appears sometimes as diffuse bright and dark zones (e.g., McLaren and Marshall 1974; Hashimoto et al. 1976; Grove 1977) or as curved boundaries resembling APB's (E. Wenk et al. 1975). If the periodic APB-structure is in contrast,  $e$ -fringes generally disappear in the vicinity of



**Fig. 2. a** Primary periodic *e*-APB pattern in labradorite Sb 1. Curved dark boundaries divide the crystal into fields. A single “dislocation” is marked by *arrow*. Notice also loops. Darkfield, *e* satellites operating. **b** Periodic *e*-APB’s in andesine Sci 1583 looking more or less edge-on to the curved boundaries corresponding to those of Fig. 2a. Notice a kink-offset in the fringe pattern and occasional single “dislocations” marked with *arrow* (for a structural interpretation compare Fig. 3). Darkfield, *e* reflections’ operating. **c** Bytownite SW 8 with zig-zag *b* boundaries (*inset*). The high magnification brightfield image illustrates the antiphase offset of (011) lattice fringes across a *b* boundary. It can best be seen by viewing along the fringe direction

these boundaries which are dark in darkfield micrographs (Fig. 2a). The dark zones have been interpreted as albite-rich regions (e.g., by McLaren and Marshall 1974). In rare cases of favorable diffraction conditions it is possible to observe fringes crossing the dark boundaries. We can then see a slight kink offset, a small change in orientation of fringes or occasionally a dislocation (Fig. 2b). The contrast of this offset in  $e$  fringes is very similar to that of *lattice fringes* across widely spaced  $b$  APB's (Fig. 2c) and we interpret them accordingly as more or less conservative APB's offsetting the  $e$ -fringe structure (Fig. 3). It is recognized that in the body-centered structure in which the fault vectors  $\mathbf{R} = \frac{1}{2}[\mathbf{c}]$  and  $\mathbf{R} = \frac{1}{2}[\mathbf{110}]$  are equivalent (Müller et al. 1973a) the distinction of conservative and nonconservative APB's is somewhat ambiguous. In cases where APB's appear as broad dark bands in which fringes are poorly resolved (e.g. Figs. 1 and 2 in Hashimoto et al. 1976) the boundaries are probably inclined and there is overlap over the thickness of the foil. Because of a reduced chance for overlap  $e$ -fringes are always more regular in thin areas of the foil and curved boundaries are generally missing.

Periodic APB's are not uncommon in metal alloy systems such as Au-Cu (e.g., Sato and Toth 1964; Chen et al. 1977), Al-Zn (Rundman and Hilliard 1967) or Ni-Mo (e.g., Ling and Starke 1971). They form during continuous ordering by a process which is analogous to spinodal decomposition at conditions of undercooling below the critical ordering temperature (e.g., Khachaturyan 1978). Continuous ordering is in contrast to ordering by nucleation and growth of ordered domains which produces smoothly curved APB's which have been documented in many minerals (Heuer and Nord 1976). Ling and Starke (1971) view it as a large wave-length compositional modulation which is convoluted and becomes increasingly dominated by a short wavelength order modulation. The orientation of APB's is determined by the elastic properties and – as in metals – the spacing of APB's in plagioclase (generally described by

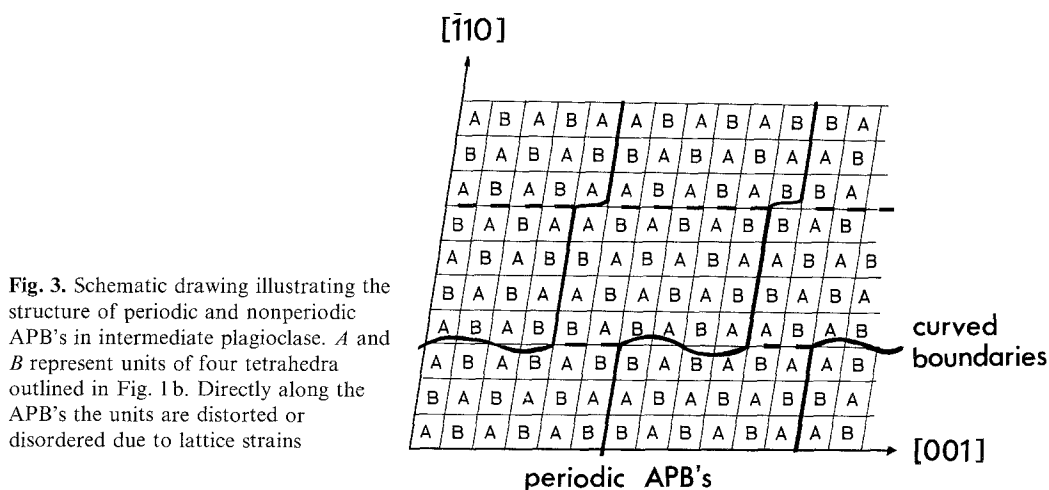


Fig. 3. Schematic drawing illustrating the structure of periodic and nonperiodic APB's in intermediate plagioclase.  $A$  and  $B$  represent units of four tetrahedra outlined in Fig. 1b. Directly along the APB's the units are distorted or disordered due to lattice strains

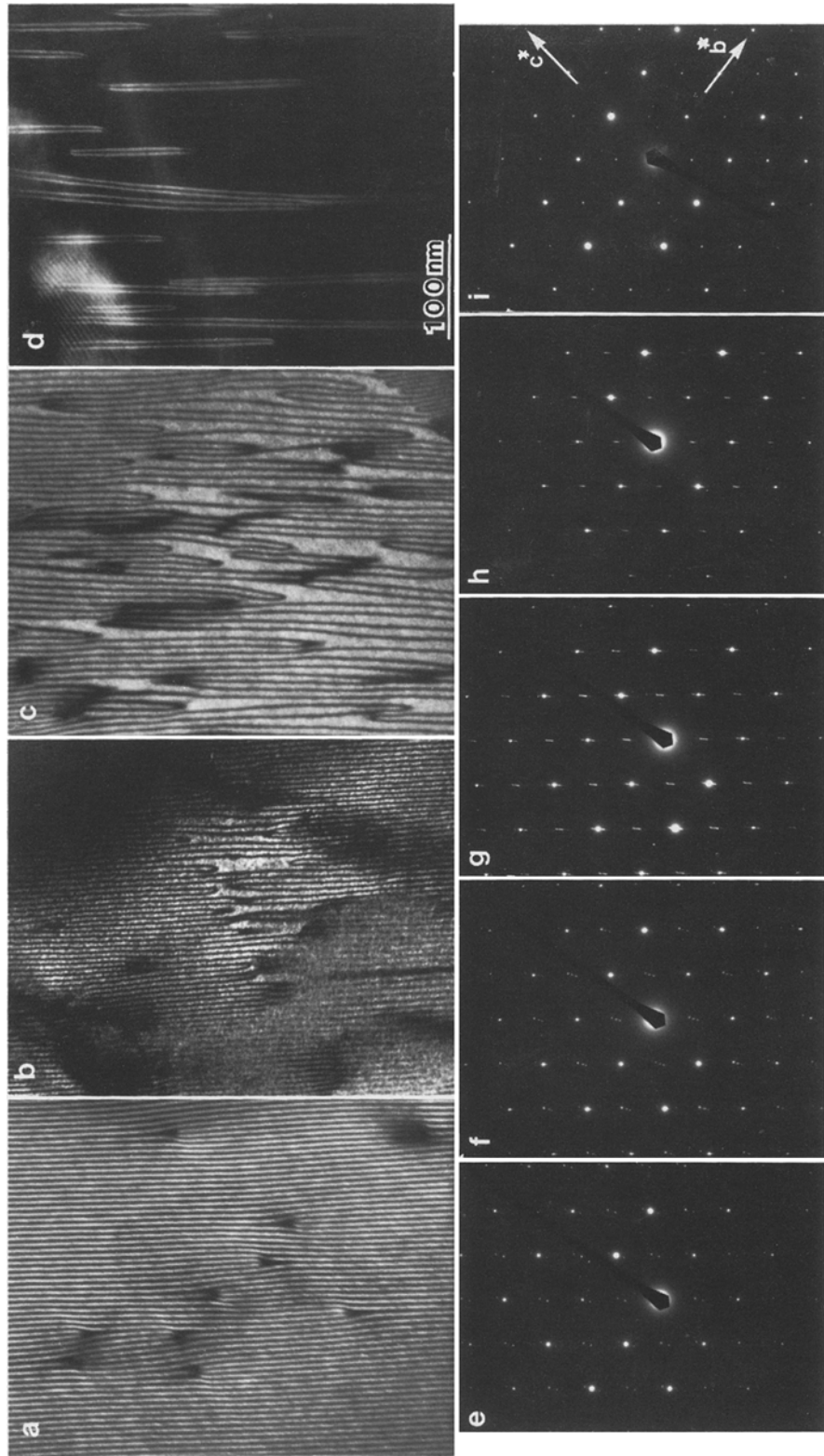
$t$  which is the distance between two  $e$  satellites in reciprocal lattice units) in a function of composition (Gay 1956) and thermal history (H.R. Wenk 1979a).

The presence of a secondary nonperiodic APB structure indicates that continuous ordering has not been strictly homogeneous throughout the crystal but started in domains with a high chance of antiphase offsets in the long period superstructure upon coincidence. Also – in contrast to classical lattice APB's – the periodic APB structure in this complex nonstoichiometric crystal often has a slightly different orientation or spacing in different parts of the crystal, producing strain contrast and occasional dislocations. Similar patterns have been observed in spinodally decomposing cubic metals where different symmetrically equivalent directions of lamellar structures within a crystal document that spinodal mechanisms operate within domains of a limited size (Wu and Thomas 1977).

### *Isochemical Decomposition of the APB Structure*

Microstructures as those described in the previous section are found in fairly rapidly cooled plutonic rocks (e.g., in anorthosites from some layered intrusions) and in metamorphic rocks which crystallized at temperatures far below the critical ordering temperature (medium and low grade amphibolite facies). Under most conditions the periodic APB structure in plagioclase does not seem to be stable. Strain energy accumulated along these closely spaced planar defects with a probability for Al–O–Al bonds is the driving force for the mobility of APB's in crystals which are annealed. The density of APB's is reduced by pairwise recombination of APB's. In a first stage adjacent APB's pinch out and form loops (Fig. 4b). Often one pair migrates out of the structure resulting in single loops in the fringe pattern with dipoles of two partial edge dislocations in the superstructure (Fig. 4a). As the decomposition proceeds the periodic fringes become more irregular and attain a wider spacing (Fig. 4c) ultimately leaving only a few stretched-out loops (Fig. 4d). This process, shown schematically in Fig. 5, is directly analogous to a decomposition of dislocation dipoles into trails of loops. Pairs of adjacent APB's of opposite sign combine and thereby annihilate which requires only short diffusion distances, on the average those between adjacent tetrahedral sites. The transformation does not require any change in bulk chemical composition (c.f. H.R. Wenk 1978). On the other hand if APB's are of equal sign recombination results in a slight local change in composition. A typical feature of recombination structures is that APB's never end within the crystal at single partial dislocations (compare with that Fig. 2a, b) but instead loop. The diffraction pattern taken on a different crystal but with similar features as in Fig. 4a shows sharp  $e$  satellites (Fig. 4e). As the structure becomes depleted in APB's additional  $b$ -reflections appear in the diffraction pattern (Fig. 4f) and when the periodic fringe pattern becomes irregular  $e$  satellites are getting diffuse (Fig. 4g) and gradually disappear (Fig. 4h) leaving a diffraction pattern with only  $a$  and  $b$  reflections corresponding to  $\bar{1}\bar{1}$  anorthite. The composition over such a profile barely changes as determined by energy-dispersive X-ray analysis in the electron microscope.





**Fig. 4. a-d** Selected darkfield micrographs illustrating secondary decomposition of the periodic APB structure by pairwise recombination. The sequence corresponds to a transition from *e* to *b* plagioclase. **a** Vz746. **b** JN03. **c** Sci 1649. **d** Vz746. **e-i** Changes in *Ok*/ electron diffraction patterns during the transition from *e* to *b* plagioclase in Spl 43f. The series is more or less equivalent to micrographs (**a-d**)

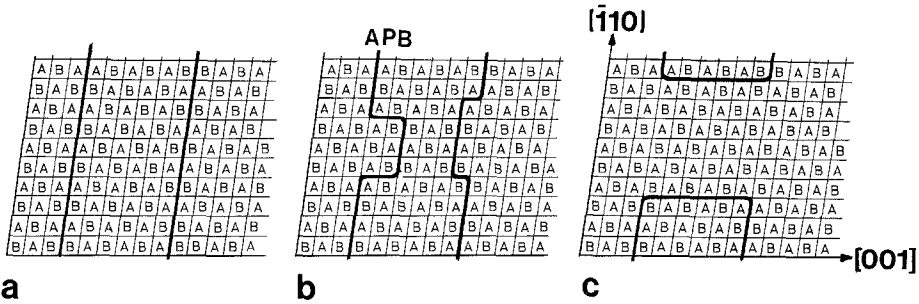


Fig. 5a-c. Schematic diagram illustrating a model for the movement of APB's resulting in a loop (c) and annihilation

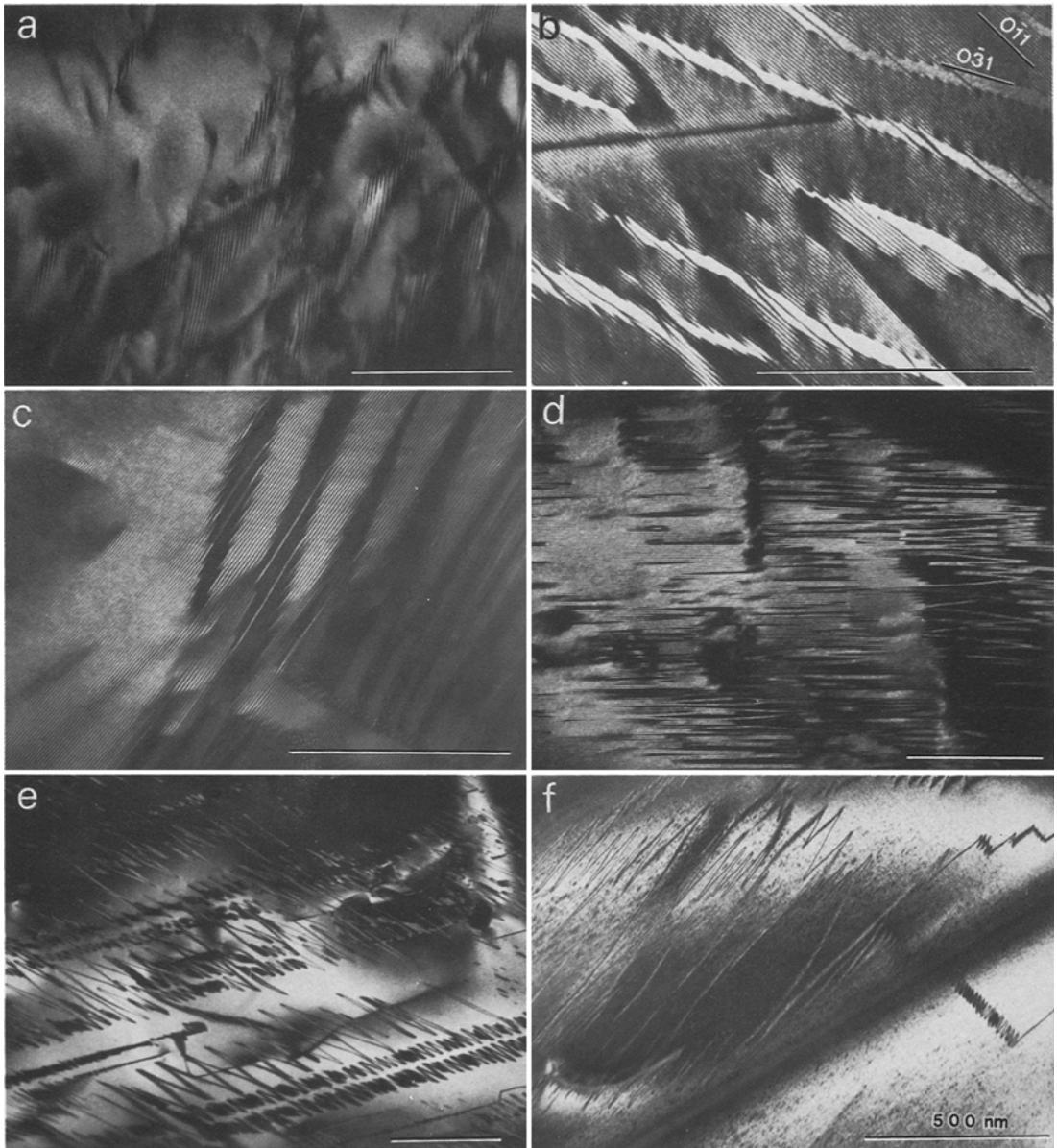
It is not clear why decomposition has rarely gone to completion and why in many crystals the original periodic APB pattern is preserved in some areas. Diffusion may be enhanced by presence of water traces and begin at grain boundaries gradually advancing into the crystal. Equilibrium is often not reached and decomposition is controlled by kinetics. In crystals with defects, stacks of APB's often remain along inclusions and along the smoothly curved APB's of Fig. 2b (compare Fig. 6b). Figure 6e, f gives examples of some advanced decompositions. If recombination and looping begins in lamellae and gradually advances into the crystal there is an equal chance to end up as a stack of loops or as meandering boundaries (Fig. 6f, lower right corner).

Some of these structures can be produced experimentally. McConnell (1974a) observed that during hydrothermal annealing of *e* plagioclase at 900 deg C *e*-satellites were replaced by *b*-reflections and he also shows presence of some loops in micrographs. Directly analogous microstructural changes have been observed and beautifully documented in heat treated Ni<sub>3</sub>Mo metal alloys (Van Tendeloo et al. 1975).

#### *Relationship of APB Microstructure and Exsolution*

In the composition range where the periodic APB structure occurs there are exsolution gaps, particularly the Huttenlocher gap in An 70–90 bytownite and the Boggild gap in An 35–65 andesine-labradorite. Exsolution in bytownites has been studied in some detail by Heuer et al. (1972), Nord et al. (1974) and Grove (1977). In contrast to those papers which emphasize chemical decomposition documented by tweed textures and lamellae, we wish to illustrate the close relationship of exsolution and the mobility of APB's as described in the previous paragraphs.

*Bytownite (Huttenlocher gap).* Figure 6a–f shows a typical series of photographs which have been taken on various *bytownite* samples. These micrographs represent a general time sequence of events during decomposition. In a first stage structures are indistinguishable from those described above. The periodic APB

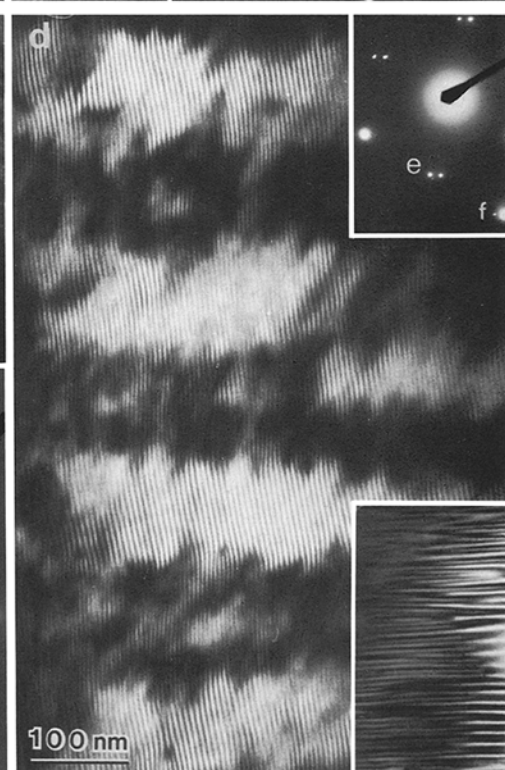
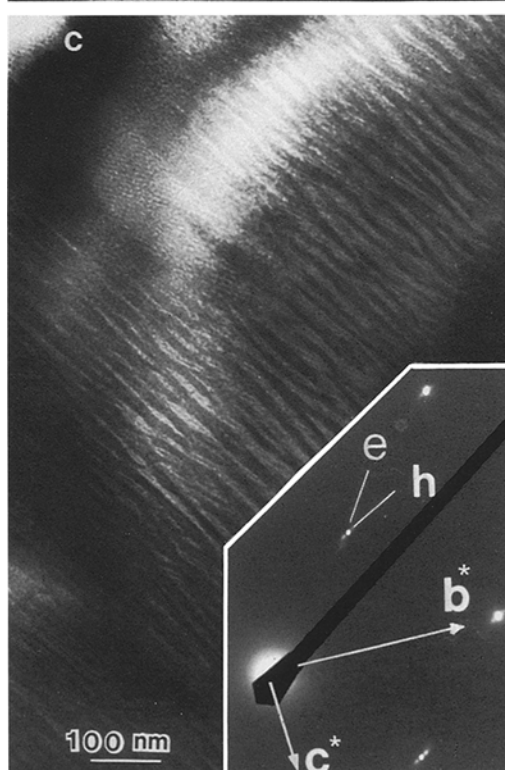
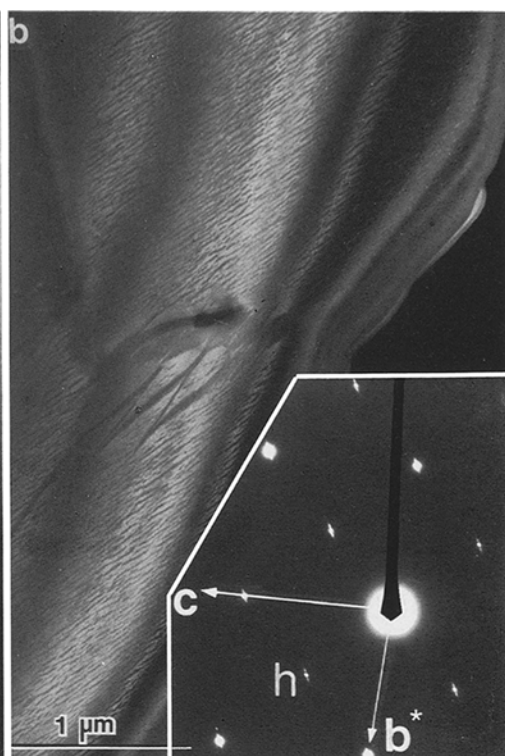
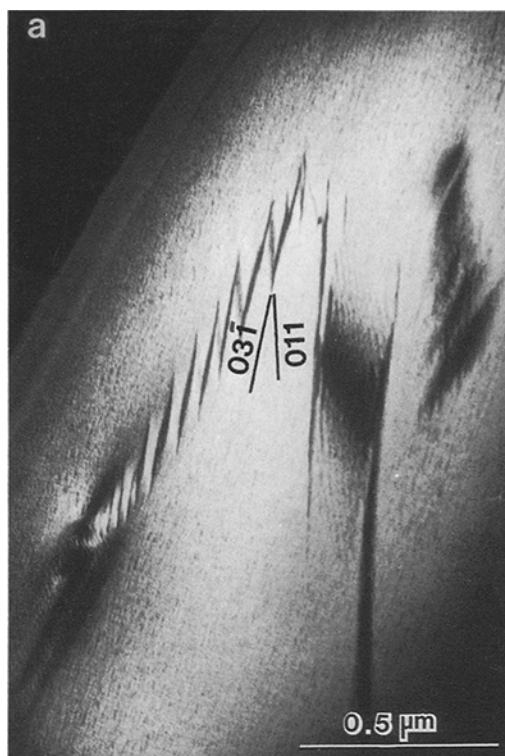


**Fig. 6a-f.** Changes in the periodic APB structure accompanied by chemical decomposition. **a, b** SLu-7. APB's recombine in inclined wedgeshaped lamellae oriented parallel to (031) which gradually coarsen. Notice that in **(b)** the periodic APB structure is preserved along one of the kink boundaries corresponding to Fig. 2b. **c** SPl 43f. Calcic part (*lower right*) is depleted in APB's except for some small stacks of loops. The *upper left corner* is more sodic and still shows the periodic *e* structure. **d** Secondary APB structure with ample looping by pairwise recombination and beginning development of zig-zag shaped boundaries (*right side*) in JN03. **e** Zig-zag *b* APB's in 984-109 which are interpreted as an end product of decomposition after wedge formation. Note how APB's are often preserved in regular stacks of loops. **f** Relic zig-zag boundaries in a Ca-rich area of JN03. Scale bar on all micrographs is 500 nm = 0.5  $\mu$ m

structure becomes irregular but, in contrast to the example in Fig. 4, lens shaped areas develop in which APB's have different orientations and spacing (Fig. 6a) suggesting compositional fluctuations. Along the boundaries there are true dislocations in the superstructure in addition to loops. As the APB structure opens up wedges develop which are characteristically inclined 10–30 deg to the fringes and oriented parallel to  $(0\bar{3}1)$  which is the direction of lamellar structures in bytownite (e.g., Huttenlocher 1942). Initially when wedges are less than 1,000 Å wide the chemical composition has not changed appreciably although this is difficult to document by direct analysis. Neither can the chemical composition be satisfactorily inferred from diffraction patterns as implied, e.g., by Grove (1977). Plagioclase with *b* reflections and plagioclase with *e*-reflections may have identical An-content depending on their thermal history. But in a later stage of coarsening internal strains in the APB depleted areas definitely cause a change in composition. These regions become gradually enriched in Ca and Al and attain a lattice geometry of anorthite. Some energy dispersive X-ray analyses in the electron microscope on areas of about 2,000 Å in diameter suggest compositional differences of up to 15 mol% An between matrix and wedges. In these wedges there are first a few widely spaced APB's (Fig. 6b–d) but most of them disappear quickly by recombination, leaving only a few isolated often zig-zag shaped boundaries (Fig. 6e, f). Zig-zag APB's can be viewed as a compromise between the original *e*-fringe direction (close to  $(0\bar{1}1)$ ) and the direction of wedges close to  $(0\bar{3}1)$  by corresponding to low energy surfaces in the crystal lattice (Nord et al. 1974). They are sometimes on a large scale but frequently they contain locally stacks of very fine loops, apparently relics of the original periodic structure. In many cases it is fairly clear that initially the plagioclase was homogeneous with a periodic intermediate plagioclase superstructure and both structural and chemical decomposition proceeded in a cooperative way.

Bytownites from of the Stillwater layered intrusion, described by Nord et al. (1974), are more complex. There is a strongly developed structure with zig-zag APB's which may have formed by a mechanism of recombination (Fig. 7a). Across these *b* boundaries we can observe an antiphase offset of  $(0\bar{1}1)$  lattice fringes at high magnification (Fig. 2c). In addition a fine regular lamellar structure is pervasive between the APB's (Fig. 7b, c). It is highly periodic with an average wavelength of 15–25 nm and gives rise to satellites in the diffraction

**Fig. 7.** a–c Microstructures in bytownites from Stillwater. **a** Zig-zag *b*-APB's in An 72, SW 5. **b** Secondary exsolution, probably by spinodal decomposition, into a fine modulated structure with characteristic "h" satellites in the SAD (*inset*) in SW 8. **c** High magnification of the modulated structure illustrating presence of *e* fringes parallel to  $(0\bar{1}1)$  in one set of lamellae. Diffraction pattern shows sharp "h" satellites due to exsolution about both *a* and *b* reflections and diffuse *e* satellites about *b* reflections. **d** Schiller labradorite from Nain (Labrador) with a bulk composition of An 53. Dark and light lamellae are interpreted as chemically different phases (one inset shows them in a low magnification image). Under some diffracting conditions *e* fringes are observed in both sets of lamellae but with different orientations and spacing, giving rise to numerous dislocations in the interface. A second inset shows the corresponding diffraction pattern with *e* and *f* reflections



pattern (Fig. 7b, inset). These “h” satellites – not described previously – occur with equal spacing about both  $a$  and  $b$  reflections and therefore are easily distinguished from  $e$  or  $f$  satellites. The lamellar structure is the product of secondary, probably spinodal, exsolution which is inhibited in the vicinity of antiphase boundaries [see also Nord et al. (1974) for Stillwater anorthosites and Grove (1977) for Nain anorthosite]. Recombination of nonconservative APB's causes local changes in chemical composition which may initiate this fine-scale exsolution (see Van Tendeloo et al. 1974). One of the exsolved phases shows sometimes intermediate plagioclase structure (Fig. 7c) resulting in a complex diffraction pattern with  $b$  reflections, diffuse  $e$  satellites (satellite vector normal to  $0\bar{1}1$ ) and “h” satellites (normal to  $0\bar{3}1$ ) (Fig. 7c, inset). Heat treatment to  $1,030^\circ\text{C}$  for 2 weeks homogenizes most of the lamellar structure and both types of satellites disappear which is in accordance with Nord et al.'s (1974) observations.

*Labradorite (Bøggild gap).* Schiller *labradorite* has been a favorite material for many TEM studies. Lamellar structures such as those shown in the inset to Fig. 7d have first been observed in the TEM by Laves et al. (1965). They correspond to lamellae which cause optical iridescence, interpreted by Laves (1960) as due to exsolution. Nissen (1971) suggested 35% and 65% An as compositions of the two exsolved phases. Schiller *labradorite* contains  $e$  satellites which can be used to image a fringe structure. Since the sodium-rich lamellae often appear as dark bands it has been suggested that those have the structure of low albite (e.g., McLaren and Marshall 1974). It is very difficult to have the  $e$  structure in contrast in both sets of lamellae because of the different irrational directions of the two satellite vectors. Occasionally diffraction conditions are obtained in which two  $e$  fringe patterns are observed which differ in orientation and spacing (Fig. 7c; see also McConnell 1974b). In order to accommodate the two structures it is necessary to introduce dislocations in the boundaries of the lamellae which renders observations more difficult. Thus at least in those samples both phases have intermediate plagioclase structure. If lamellae are wide then in addition to the periodic APB's secondary curved boundaries are present (see e.g. Fig. 1a in Hashimoto et al. 1976). This suggests that APB structures in Schiller *labradorite* formed contemporaneously with exsolution and there is little evidence for secondary modification by recombination in contrast to bytownite.

*Albite-Anorthite.* An interesting special case is an *albite-anorthite* intergrowth resulting from decomposition of andesine (H.R. Wenk 1979b). This unusual assemblage has been found in amphibole schists from low amphibolite facies metamorphic grade. The homogeneous APB structure of andesine becomes locally distorted. In one region it opens up by pairwise recombination of APB's to pure anorthite (An 95) which only shows a few isolated  $b$  boundaries (Fig. 5 in H.R. Wenk 1979b). In another region of the same crystal the periodic APB structure attains a closer fringe spacing and over a few hundred Angstroms the intermediate structure transforms to pure albite (An < 5) without a superstructure.

## Discussion

The observations of APB microstructure in intermediate plagioclase documents a high mobility of antiphase boundaries. The continuous transition between *e* plagioclase and *b* plagioclase are perhaps the strongest support yet for a model of intermediate plagioclase which emphasizes stacking of basic building units. Even in a stacking model the structure may be considerably distorted along the APB's due to internal strains. The way in which periodic *e* fringes are eliminated by pairwise recombination demonstrates that they are basically antiphase boundaries which are not stable under most geological conditions, i.e., they have a positive surface energy. Plagioclase structures with APB's including *e* plagioclase are therefore of a transient nature. If they are annealed at a sufficiently high temperature they become depleted of APB's. This changes the geometry of the APB pattern and particularly the average wavelength of the modulation. The transition can be observed directly in darkfield images but it can also be inferred from diffraction patterns which change continuously from *e* plagioclase with satellites to *b* plagioclase with simple superreflections. Use of the *t* satellite vector for determinative purposes for chemical composition and temperature of formulation, e.g., by Gay (1956) and H.R. Wenk (1979a) is only valid if it is measured in those areas of the crystal which have not undergone recombination. This has to be established by electron microscopy particularly by verifying absence of looping APB's. It is conceivable that under certain conditions APB's are stable and have negative surface energy. Zig zag boundaries in Stillwater plagioclase could possibly be the result of APB growth increasing their surface area on low energy planes instead of a final product of decomposition.

Displacements of APB's are accomplished by movements of partial dislocations and do not require any large scale diffusion or chemical decomposition. But APB's seem to provide favorable surfaces for more extensive Al—Si and Ca—Na diffusion and exsolution in the bytownite and labradorite composition ranges and are influential in the chemical decomposition of plagioclase. Ordering and exsolution are thus cooperative processes. The dominating influence may change in space and time and is largely controlled by local kinetics.

Even without a quantitative understanding of ordering kinetics the APB structure provides important information on both temperatures of crystallization and the subsequent thermal history of plagioclase which permits us to further characterize high grade metamorphic and igneous rocks. In an earlier publication we have used a TTT diagram to represent processes occurring during ordering of calcic plagioclase (Fig. 8 in H.R. Wenk et al. 1980) which may be useful to consult during this discussion of representative microstructures. We can distinguish between primary and secondary structures. Among the former there is a division into curved generally widely spaced APB's and periodic APB's. *Curved APB's* are typical of volcanic rocks which cooled moderately quickly from high temperatures (1,100°–1,200° C; see Christie et al. 1971; Grove 1977). There is very little crystallographic control on these boundaries which are observed in  $\text{I}\bar{\text{I}}$  plagioclase with An contents of 60 and higher and more rarely in  $\text{P}\bar{\text{I}}$  anorthite

with sharp *c* reflections. There is no evidence for significant boundary mobility. *Periodic APB* structures are found in metamorphic rocks recrystallizing at moderate temperatures (500°–800° C) and in many plutonic rocks which cooled slowly. In primary fringe structures the pattern is regular in domains 50–100 nm wide, but interrupted by curved boundaries. Spacing and orientation of fringes is a function of composition and temperature of formation. Upon annealing at high temperatures of granulite or high grade amphibolite facies and during retrograde metamorphism APB's become mobile. In a first stage curved boundaries separating domains disappear through adjustment of the periodic APB's and in a second stage periodic APB's begin to combine and annihilate. APB's generally have strong preferential orientation during most stages of decomposition. Stretched-out loops, single pairs and zigzag boundaries are often observed. Zigzag APB's are particularly common in bytownites which underwent exsolution. Given sufficient time and high enough temperature of annealing structures become depleted in APB's and end up as *b* plagioclase that may be structurally and chemically indistinguishable from *b* plagioclase which formed by nucleation and growth.

The observations presented in this paper thus lead us to a physico-chemical model for the origin of APB structures which is quite different from that of Grove (1977) summarized on a phase diagram (his Fig. 13). Without specifying mechanisms Grove views all *e*- and *b* plagioclase as due to phase transformations from high albite ( $C\bar{1}$ ). According to him, there are stability fields for *e* plagioclase and *b*-plagioclase with a boundary at An 75.

Our data supports a model in which *b* plagioclase is the stable phase over a much larger composition field at least to An 65 and the formation of *e* or *b* plagioclase is dependent on kinetics rather than thermodynamics. *b* Plagioclase forms at high temperature from a disordered phase or during crystallization (Kroll and Müller 1980) and at lower temperatures during annealing from *e* plagioclase which is also in agreement with McConnell's (1974) heating experiments. It is still unresolved whether disordered calcic plagioclase ever has a high albite  $C\bar{1}$  structure or if it consists of randomly stacked units in which Al and Si are at least short-range ordered (H.R. Wenk et al. 1980).

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