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A Review of the Recent Literature published up to mid-1977

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Preface

CHEMICAL PHYSICS OF SOLIDS AND THEIR SURFACES

The first six volumes of this series were published under the title 'Surface and Defect Properties of Solids'. Our reasons for the change of heading are simple. Although, as Senior Reporters and Contributors, we are still of the opinion that much of chemical interest in the study of the solid state is encompassed by the title we originally chose, we recognise that there are certain important topics and phenomena, of direct interest to a wide audience, that are better described by the new title. The 'atom-atom potential' approach to the unification of organic solid state chemistry (one of the topics discussed at length in this volume by Ramdas and Thomas) is a case in point. A second important reason which, with hindsight, we now more fully appreciate, is that the original title did not, for one reason or another, arouse the curiosity of many chemical physicists and others in interdisciplinary areas. We shall not abandon our interest in the chemical and other consequences of structural imperfections – indeed no comprehensive approach to the phenomenology of solids can afford to do so – but we shall increase the area of the canvas that we propose to cover by adopting our new title. In so doing we hope to bring together the wide spectrum of experts upon whose services we have been fortunate to prevail in the past. Such an approach integrates rationally the systematic study of surface and bulk properties, irrespective of whether or not the latter are associated with crystalline defects. As in preceding issues, we propose to continue with the selective rather than the comprehensive approach.

The opening chapter by McLaren on the microstructures of feldspars, takes up the theme pursued at some length by Hutchinson, Jefferson, and Thomas in Vol. 6 in their review of the electron microscopic study of minerals (excluding feldspars). This is a field which has many implications for mineralogists, geochemists, and solid state physicists.

Cluster chemistry is currently of great academic and industrial importance. Quite apart from the insight into bonding that these metal cluster carbonyl compounds afford, they exhibit, at least in their partially decomposed state (see *J.C.S.Chem. Comm.*, 1978, 566) remarkable catalytic activity which, *inter alia*, may be harnessed to produce the lower alcohols from mixtures of hydrogen and carbon monoxide. The balanced review of Takasu and Bradshaw is, therefore, timely.

Neutron scattering from adsorbed molecules and intercalates is treated for the first time in this series by Hall and Wright. This is a field that is likely to grow rapidly after a decade of quiet anticipation, the last review having been published some ten years ago. The sixth chapter is concerned with photo-induced reactivity at oxide surfaces, and Bickley, not unnaturally, dwells largely on information obtained with two oxides, ZnO and TiO₂. In the final chapter Pritchard discusses in depth the present state of the application of infrared reflection spectroscopy to chemisorption on clean metal surfaces.

J. M. Thomas
M. W. Roberts

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Defects and Microstructures in Feldspars

BY A. C. McLAREN

1 Introduction

The minerals of the feldspar group are probably the most important of all rock-forming substances since they make up between 50 and 60 weight per cent of all igneous rocks and, in addition, they occur under a wide range of geological conditions. In fact, the classification of rocks is based to a large extent on the quantity and kinds of feldspars present.

In view of this, the feldspars have been studied in greater detail than any other group of minerals. The literature is, therefore, voluminous but fortunately there are good summaries in many elementary text books on mineralogy,¹ as well as more extended reviews.²⁻⁴ In addition, there is the monumental work by J. V. Smith.⁵

Optical microscopy and X-ray diffraction studies in particular have shown that the feldspars are an extremely complicated group of minerals and that specimens as we find them are very rarely homogeneous single crystals with grown-in or stress-induced crystals defects such as dislocations and twins. In general, feldspar specimens consist of a complex microstructure which is the product of order-disorder and structural transformations, as well as diffusion controlled processes such as exsolution (solid state precipitation). In addition, feldspar specimens which have been strained (deformed) in response to externally applied stresses develop characteristic microstructures.

Before proceeding further it is necessary to consider briefly the nature of the feldspar series of minerals and their basic crystal structure.

The feldspars fall into two main series: (i) the alkali feldspars KAlSi_3O_8 to $\text{NaAlSi}_3\text{O}_8$ and (ii) the plagioclase feldspars $\text{NaAlSi}_3\text{O}_8$ to $\text{CaAl}_2\text{Si}_2\text{O}_8$. These end members are referred to as orthoclase (Or), albite (Ab), and anorthite (An), respectively.

The chemical composition of any feldspar mineral is usually given in terms of the mol per cent of Or, Ab, and An. The alkali feldspars usually contain less than 10 per cent An, but the Na-rich members (such as anorthoclase) may contain more. Similarly, the plagioclase feldspars usually contain less than 10 per cent Or. The composition of any specimen is written as $\text{An}_x\text{Ab}_y\text{Or}_z$ where x , y , and z are the concentrations in mol per cent.

The feldspar structure is based on a framework of $(\text{Al,Si})\text{O}_4$ tetrahedra, with the

¹ M. H. Battey, 'Mineralogy for Students', Oliver and Boyd, Edinburgh, 1972.

² W. A. Deer, R. A. Howie, and J. Zussman, 'Rock-Forming Minerals, Vol. 4, Framework Silicates', Longmans, London, 1963.

³ T. F. W. Barth, 'Feldspars', Wiley-Interscience, New York, 1969.

⁴ Mineralogical Society of America, Short Course Notes Vol. 2, Feldspar Mineralogy, ed. P. H. Ribbe, 1975.

⁵ J. V. Smith, 'Feldspar Minerals', Vols. 1 and 2, Springer-Verlag, Berlin, 1974.

metal ions (K, Na, Ca) occupying positions in the interstices of the framework. The idealized feldspar structure is monoclinic with space group $C2/m$ and there is complete disorder in the occupancy of tetrahedral sites by Al and Si. This is the structure of the K-rich mineral sanidine which has $4 \text{ KAlSi}_3\text{O}_8$ per unit cell. However, the fully ordered structure of KAlSi_3O_8 is triclinic, with space group $C\bar{1}$. This mineral is known as (maximum) microcline and has a structure similar to that of low-temperature fully ordered albite.

With the exception of monalbite (a high-temperature, monoclinic, disordered form of albite), the plagioclase feldspars are all triclinic. Because the Al/Si ratio in anorthite (An_{100}) is 1:1, ordering requires a regular alternation of Al and Si in the framework and this produces a body-centred structure $I\bar{1}$ with a doubled c -axis. For this reason, it is usual when considering the plagioclase series to use this larger unit cell containing eight formula units.

The structural type exhibited by any particular feldspar specimen and its unit cell dimensions are clearly a function of the chemical composition and the degree of ordering which itself is dependent upon the temperature of crystallization and the subsequent thermal history of the specimen. For example, feldspars in volcanic rocks which have crystallized at high temperature followed by quenching to a low temperature may retain their high-temperature disordered state. On the other hand, feldspars in rocks which have cooled slowly may become ordered into a low-temperature state.

However, when any feldspar specimen is cooled from a high temperature, other significant changes may also occur, as indicated above. It is these changes, together with changes directly related to ordering, which are responsible for the microstructures observed. Sometimes the microstructure is on a coarse enough scale for it to be observed directly by optical microscopy. For example, alkali feldspar specimens of intermediate composition which are homogeneous at high temperatures, exsolve at low temperatures into periodically-twinned domains of Na-rich feldspar and untwinned-domains of K-rich feldspar. On the other hand, the existence in some specimens of microstructures of exsolution and/or twinning on a very fine scale was implied originally from X -ray observations. But such observations provide little or no information about the size, shape, and distribution of the domains.

The first successful use of transmission electron microscopy to obtain such information on an alkali feldspar was made by Fleet and Ribbe.⁶ They showed that a K-rich moonstone from Ceylon consisted of alternating lamellae of monoclinic orthoclase and triclinic albite approximately parallel to $(\bar{6}01)$. The lamellae were of the order of 1000 \AA wide and the albite lamellae were periodically twinned on the albite-twin law. These observations gave a detailed explanation of the features of the associated diffraction pattern and further explained the origin of the well-known 'schiller' (or interference colours) exhibited by moonstone.

These observations were, of necessity, made on the thin edges of tiny crushed fracture fragments of the moonstone. In spite of the obvious disadvantages of this method of specimen preparation, many useful TEM studies of feldspars and other minerals were made. However, most of these disadvantages have been overcome by the development of ion-bombardment thinning. With this technique it became possible to produce consistently extensive thin areas of a wide range of non-metallic materials, and to relate TEM and optical microscope observations directly. As a

⁶ S. G. Fleet and P. H. Ribbe, *Phil. Mag.*, 1963, 8, 1179.

consequence, there has been a spectacular increase in the application of TEM to mineralogical and petrological problems.⁷ McLaren⁸ has reviewed the TEM observations of feldspars which had been carried out up to the beginning of 1972. Since then a number of important observations have been made. In the plagioclase feldspars extensive work has been carried out on (i) antiphase domains;⁹⁻¹⁶ (ii) the coexistence of domains of different structural type;^{14,15} (iii) exsolution;^{15,17-19} (iv) the occurrence and nature of the superlattice structure in specimens of intermediate composition ($An_{2.5}$ to $An_{7.5}$);^{8,15,18-24} and (v) crystal defects and their role in the mechanisms of deformation.²⁵⁻³²

Work on the alkali feldspars has been almost exclusively concerned with exsolution phenomena, in particular spinodal decomposition and its growth into incoherent precipitates, together with the role of twinning in reducing stress.^{8,33-38} Most of

- ⁷ 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976.
- ⁸ A. C. McLaren, 'The Feldspars', ed. W. S. MacKenzie and J. Zussman, Manchester University Press, Manchester, 1974, p. 378.
- ⁹ J. M. Christie, J. S. Lally, A. H. Heuer, R. M. Fisher, D. T. Griggs, and S. V. Radcliffe, *Geochim. Acta*, 1971, Suppl 2, 1.
- ¹⁰ A. H. Heuer, J. S. Lally, J. M. Christie, and S. V. Radcliffe, *Phil. Mag.*, 1972, **26**, 465.
- ¹¹ W. F. Müller, H.-R. Wenk, and G. Thomas, *Contrib. Mineral. and Petrol.*, 1972, **34**, 304.
- ¹² W. F. Müller, H.-R. Wenk, W. L. Bell, and G. Thomas, *Contrib. Mineral. and Petrol.*, 1973, **40**, 63.
- ¹³ G. L. Nord, A. H. Heuer, and J. S. Lally, 'The Feldspars', ed. W. S. MacKenzie and J. Zussman, Manchester University Press, Manchester, 1974, p. 378.
- ¹⁴ A. C. McLaren, *Contrib. Mineral. and Petrol.*, 1973, **41**, 47.
- ¹⁵ A. C. McLaren and D. B. Marshall, *Contrib. Mineral. and Petrol.*, 1974, **44**, 237.
- ¹⁶ A. H. Heuer, G. L. Nord, J. S. Lally, and J. M. Christie, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 345.
- ¹⁷ G. Cliff, P. E. Champness, H.-U. Nissen, and G. W. Lorimer, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 258.
- ¹⁸ T. L. Grove, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 266.
- ¹⁹ H.-U. Nissen, 'The Feldspars', ed. W. S. MacKenzie and J. Zussman, Manchester University Press, Manchester, 1974, p. 491.
- ²⁰ J. D. C. McConnell, 'The Feldspars', ed. W. S. MacKenzie and J. Zussman, Manchester University Press, Manchester, 1974, p. 478.
- ²¹ E. H. Slimming, *Amer. Mineral.*, 1976, **61**, 54.
- ²² H. Hashimoto, H.-U. Nissen, A. Ono, A. Kumao, H. Endoh, and C. F. Woensdregt, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 332.
- ²³ M. Kitamura and N. Morimoto, *Phys. Chem. Minerals*, 1977, **1**, 199.
- ²⁴ Y. Nakajima, N. Morimoto and M. Kitamura, *Phys. Chem. Minerals*, 1977, **1**, 213.
- ²⁵ G. W. Lorimer, H.-U. Nissen, and P. E. Champness, *Schweiz. Mineral. Petrogr. Mitt.*, 1974, **54**, 707.
- ²⁶ D. B. Marshall and A. C. McLaren, 'Eighth International Congress on Electron Microscopy', Canberra, 1974, **1**, 490.
- ²⁷ S. White, *Contrib. Mineral. and Petrol.*, 1975, **50**, 287.
- ²⁸ D. B. Marshall, R. H. Vernon, and B. E. Hobbs, *Contrib. Mineral. and Petrol.*, 1976, **57**, 49.
- ²⁹ D. B. Marshall and C. J. L. Wilson, *Contrib. Mineral. and Petrol.*, 1976, **57**, 55.
- ³⁰ D. B. Marshall and A. C. McLaren, *Phys. Chem. Minerals*, 1977, **1**, 351.
- ³¹ D. B. Marshall and A. C. McLaren, *J. Materials Sci.*, 1977, **12**, 893.
- ³² D. B. Marshall and A. C. McLaren, *Phys. Stat. Solidi (A)*, 1977, **41**, 231.
- ³³ D. C. Owen and J. D. C. McConnell, 'The Feldspars', ed. W. S. MacKenzie and J. Zussman, Manchester University Press, Manchester, 1974, p. 424.
- ³⁴ R. A. Yund, A. C. McLaren, and B. E. Hobbs, *Contrib. Mineral. and Petrol.*, 1974, **48**, 45.
- ³⁵ W. L. Brown and C. Willaime, 'The Feldspars', ed. W. S. MacKenzie and J. Zussman, Manchester University Press, Manchester, 1974, p. 440.
- ³⁶ C. Willaime, W. L. Brown, and M. Gandais, *J. Materials Sci.*, 1973, **8**, 461.
- ³⁷ C. Willaime, W. L. Brown, and M. Gandais, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 248.
- ³⁸ G. W. Lorimer and P. E. Champness, *Phil. Mag.*, 1973, **28**, 1391.

this work was done on alkali feldspars in the composition range from about $\text{Or}_{30}\text{Ab}_{70}$ to about $\text{Or}_{70}\text{Ab}_{30}$, and many details of the nature of the observed microstructures and their origin are now well understood.

However, in spite of an extensive background of optical microscope and X-ray studies, only two TEM studies have been made recently on specimens outside this composition range where microstructures associated with the monoclinic to triclinic transition are expected to be conspicuous. Both these studies were concerned with microcline ($\text{Or}_{90\pm 10}$) and they must be considered, essentially, as preliminary.^{39,40}

It would, I believe for two reasons, be inappropriate and, indeed, unnecessary to attempt a comprehensive review of all these observations here. Firstly, the true significance of much of the TEM work cannot be appreciated without an understanding of the mineralogical background which needs to be developed in some detail for each particular problem. Secondly, excellent and critical reviews covering much work done over the last five years have recently been given by Heuer and Nord,⁴¹ Champness and Lorimer,^{17,42} Yund,⁴³ Ribbe,⁴⁴ and, of course, J. V. Smith.⁵ The problem here has been to select those topics for discussion which will produce a review whose character is (i) sufficiently synoptic to interest a wide range of materials scientists (chemists, physicists, mineralogists, and geologists) in the application of TEM to solid state problems and (ii) sufficiently seminal to interest people actively engaged in feldspar research.

In an attempt to satisfy these criteria I have decided to restrict this review to a detailed discussion of two problems of current interest, each showing clear evidence for the necessity of further work. The first of these problems is concerned with the nature of the superlattice structure responsible for the *e*- and *f*-reflections in the plagioclase feldspars of intermediate composition (*e*-plagioclases). The most recent work on this problem has involved the use, for the first time in feldspar research, of high-resolution lattice-imaging techniques. The second problem is concerned with the defects and microstructures associated with the monoclinic to triclinic transition in the alkali feldspars. This work is particularly concerned with transformation twinning and exsolution in microcline ($\text{Or} > 80$ per cent) and anorthoclase ($\text{Or} < 30$ per cent), and illustrates the combined use of conventional optical and electron microscope techniques.

2 The Structure of *e*-Plagioclase

High-resolution lattice-imaging TEM has recently been applied to the long-standing problem of the nature of the *e*-plagioclases. In this section an attempt will be made to review these observations critically in the light of earlier work using TEM and X-ray diffraction. However, this must be preceded by some background mineralogical

³⁹ M. Akizuki, *Amer. Mineral.*, 1972, 57, 797.

⁴⁰ J. E. Tibbals and A. Olsen, *Phys. Chem. Minerals*, 1977, 1, 313.

⁴¹ A. H. Heuer and G. L. Nord, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 274.

⁴² P. E. Champness and G. W. Lorimer, 'Electron Microscopy in Mineralogy', ed. H.-R. Wenk, Springer-Verlag, Berlin, 1976, p. 174.

⁴³ R. A. Yund, 'Mineralogical Society of America, Short Course Notes, Vol. 2, Feldspar Mineralogy', 1975, Ch. 5 and 6.

⁴⁴ P. H. Ribbe, 'Mineralogical Society of America, Short Course Notes, Vol. 2, Feldspar Mineralogy', 1975, Ch. 1 and 8.

and crystallographic considerations, as well as a discussion of the microstructures of specimens with the *e*-plagioclase structure.

Background.—²⁻⁵The plagioclase feldspars exhibit three basic structural types: (i) the albite structure $C\bar{1}$ with *a*-reflections ($h + k = 2n$; $l = 2n$) only, (ii) the body-centred structure $I\bar{1}$ with *a*-reflections and *b*-reflections ($h + k = 2n + 1$; $l = 2n + 1$), and (iii) the primitive structure $P\bar{1}$ with *c*-reflections ($h + k = 2n$; $l = 2n + 1$) and *d*-reflections ($h + k = 2n + 1$; $l = 2n$) in addition to *a*- and *b*-reflections. Also, there is the superlattice (or *e*-plagioclase) structure which is characterized by pairs of *e*-reflections in place of *b*-reflections, and *f*-reflections as satellites to *a*-reflections. There are no *c*- or *d*-reflections. A typical diffraction pattern is shown in Figure 1. McLaren⁸ has analysed this diffraction pattern and shown that both the *e*- and *f*-reflections are due to a superlattice with period $T = 1/|t|$; where *t* is the reciprocal lattice vector giving the position of an *f*-satellite relative to the associated *a*-reflection. Vector *t* also defines the position of one *e*-reflection of a pair relative to the other *e*-reflection.

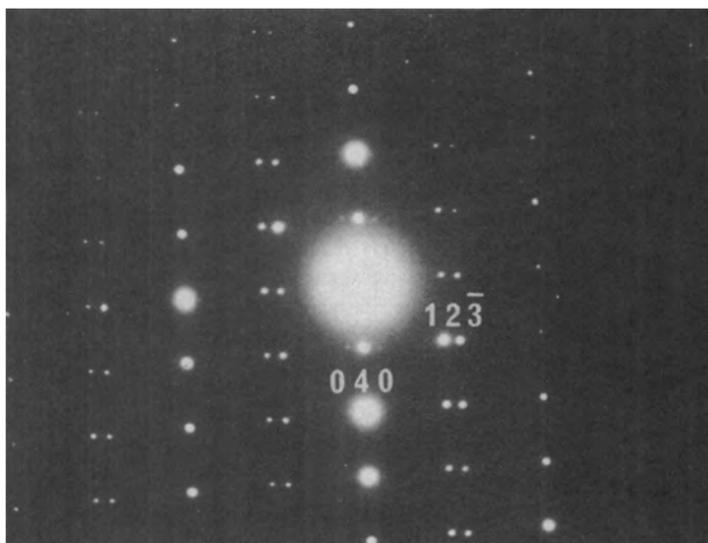


Figure 1 Selected area electron diffraction pattern of a specimen of composition An_{32} . The electron beam is normal to (100). Note the pairs of *e*-reflections and the weak *f*-reflections characteristic of the *e*-plagioclases

This superlattice structure is observed only in specimens in the intermediate composition range (An_{25} to An_{75}) which have been cooled slowly from high temperatures. Both the magnitude and direction of *t* vary with An-content. These variations were first determined from X-ray diffraction patterns,^{4,5} but electron diffraction²¹ has recently been used to obtain more accurate measurements over the range An_{34} to An_{69} in a cogenetic series of specimens. When the direction of *t* is plotted on a stereographic projection, the observations for various An-contents lie,

^{4,5} M. G. Bown and P. Gay, *Z. Krist.*, 1958, **111**, 1.

in general, on a great circle. Similarly, the observed values of the magnitude of t as a function of An-content lie approximately on a straight line. However, there is evidence to suggest that t does not vary continuously across the intermediate plagioclase range, there being a discontinuity at a composition of about An₅₀. Also, the *rate of change* with An-content of both the magnitude and direction of t increases with higher An-content. Thus, any error in the An-content will introduce a greater uncertainty in t for specimens of higher An-content. Both the direction and magnitude of t observed by McLaren⁸ in An₇₅ have been questioned,⁵ but they are smooth extrapolations of the curves quoted above, $T = 1/|t|$ being 85 Å. In a specimen of estimated composition An₇₂, Heuer and Nord (personal communication) found $T = 96$ Å, which is certainly much higher than expected. On the other hand, Grove⁴⁶ quotes values of T as low as 37 Å in specimens of An₇₆. It is clear that at compositions around An₇₅ there is considerable uncertainty about the magnitude and direction of t .

The problem with e -plagioclases is a two-fold one: Firstly it is necessary to determine the basic structure, and secondly to understand the observed variation of t with An-content. However, before going on to consider the structure, it is necessary to investigate the microstructure of specimens which exhibit the characteristic diffraction pattern.

Microstructure.—The two specimens showing the e -plagioclase diffraction pattern which have been examined by high-resolution lattice-imaging TEM^{22,24} are both schiller labradorites with compositions of An₅₄ and An₅₂. The microstructure of similar specimens has also been examined in detail by TEM, and these observations will now be discussed.

Although there is no evidence in normal X -ray or electron diffraction patterns for exsolution in these specimens, TEM has revealed the existence of a microstructure consisting of two kinds of alternating lamellae⁸ of thicknesses of the order of 1000 Å. It is this microstructure which is responsible for the interference colours or Schiller exhibited by these specimens. Subsequent observations¹⁷ using the analytical electron microscope have shown that the lamellae differ in composition by about 12 per cent An.

The lamellae may be visible in bright-field (BF) images but they are better seen and more easily analysed in dark-field (DF) images. The diffraction contrast of the lamellae in DF images with a -reflections has been studied in detail by McLaren⁸ and it was shown that the contrast arises because of a slight misorientation between adjacent lamellae. When the crystal is in the symmetrical position on the rocking curve (*i.e.* when the mean deviation from the exact Bragg angle $\bar{s} = 0$) the contrast is extremely weak and there is a reversal of contrast with the sign of \bar{s} , as occurs across a bend contour. It was also found that one set of lamellae (A) is consistently wider than the other set (B). The observed contrast indicates that the intensities of a -reflections in A and B [and hence the structure factors $F_a(A)$ and $F_a(B)$] are not significantly different at $s = 0$.

However, this is not so for e -reflections.¹⁵ It can be seen from the DF image of Figure 2 that the diffraction contrast is extremely strong at $s = 0$. The A and B lamellae are bright and dark, respectively. There is no reversal of contrast with the sign of s . This indicates that the structure factors for e -reflections, $F_e(A)$ and $F_e(B)$, are significantly different, in fact it appears that $F_e(B) = 0$. It follows that the 30 Å

⁴⁶ T. Grove, *Contrib. Mineral. and Petrol.*, 1977, **64**, 273.

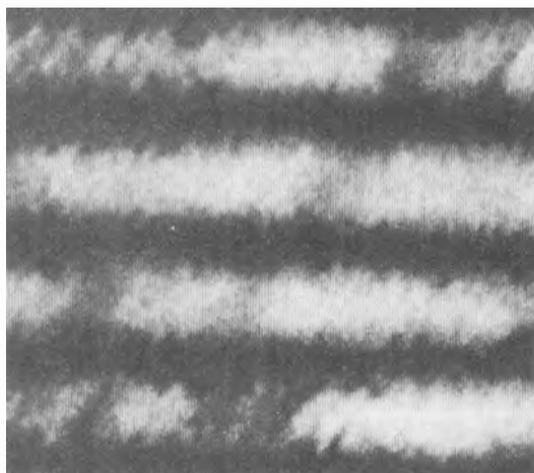


Figure 2 The Schiller lamellae in a specimen of labradorite An_{52} imaged in DF with the $(12\bar{3})$ pair of e -reflections. The plane of the specimen is (100) , and the lamellar-period is approximately 1200 \AA .

superlattice associated with the e - and f -reflections should be observed in A-lamellae only. This has been confirmed by the direct resolution of the superlattice (i) using a pair of e -reflections as in Figure 3 and (ii) using the $0\bar{2}0, 000, 020$ and the six associated f -reflections as in Figure 10 of McLaren.⁸ Since no (unsplit) b -reflections are observed in the diffraction patterns, it must be concluded that the B-lamellae have the high-temperature (disordered) structure $C\bar{1}$.

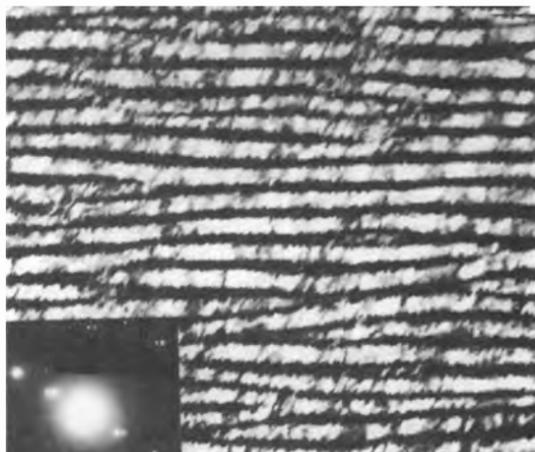


Figure 3 The 30 \AA superlattice in a (100) plate of An_{52} imaged with the $(12\bar{3})$ pair of e -reflections

The high contrast achieved in DF images using a pair of e -reflections reveals much more detail of the structure of the Schiller lamellae than is observed in DF images with a -reflections. From Figures 2 and 3 it can be seen that the B-lamellae consist of walls of small, irregularly shaped domains of the $C\bar{I}$ structure (dark contrast). This has also been observed by McConnell²⁰ and Nissen (personal communication). The lamellar-boundaries are not planar. Occasionally bright patches (in which the superlattice is resolved) are seen *within* the dark B-lamellae. Also there are often grey regions within the A-lamellae which are presumably $C\bar{I}$ domains which are thinner than the thickness of the crystal. This interpretation is supported by observations on an (010) slice. This plane is almost parallel to the plane of the Schiller lamellae and in the DF image (using a pair of e -reflections) shown in Figure 4, it will be seen that the microstructure now appears as an apparently random distribution of $C\bar{I}$ domains (200–500 Å in size).

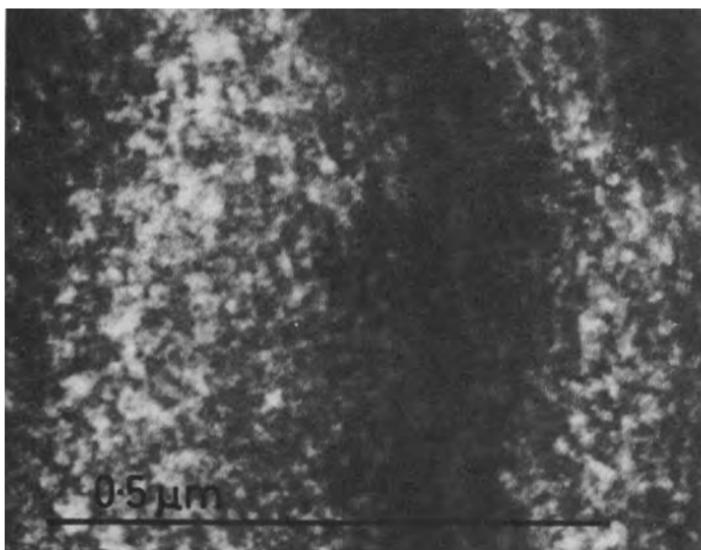


Figure 4 DF electron micrograph on a pair of e -reflections showing the domain structure observed in an (010) plate of specimen An_{32} . The 30 Å superlattice is resolved

McLaren and Marshall¹⁵ also examined a specimen of composition An_{32} which exhibited the characteristic e -plagioclase diffraction pattern (with very weak f -reflections), but no Schiller. DF images using a -reflections showed no significant microstructure. However, DF images with a pair of e -reflections showed a random distribution of dark domains (presumably with the $C\bar{I}$ structure) and bright domains in which the 22 Å superlattice characteristic of this composition was resolved.

High-resolution, Lattice-imaging TEM.—The superlattice associated with the e - and f -reflections must arise from the ordering of some kind of point, line or planar defects. However, it is clear that direct resolution of the superlattice alone provides no information about the nature of the structure.

The first attempt¹⁵ to obtain such information from a series of one-dimensional lattice images produced no evidence for the type of antiphase structures based on the original model of Chao and Taylor⁴⁷ (see below). However, Hoshimoto *et al.*²² and Nakajima *et al.*²⁴ have succeeded in obtaining 2-dimensional lattice images showing an antiphase structure. An example from Nakajima *et al.*²² is shown in Figure 5. The electron beam is parallel to [311]. The superlattice period of about 31 Å (characteristic of this composition) is clearly observed and is normal to the

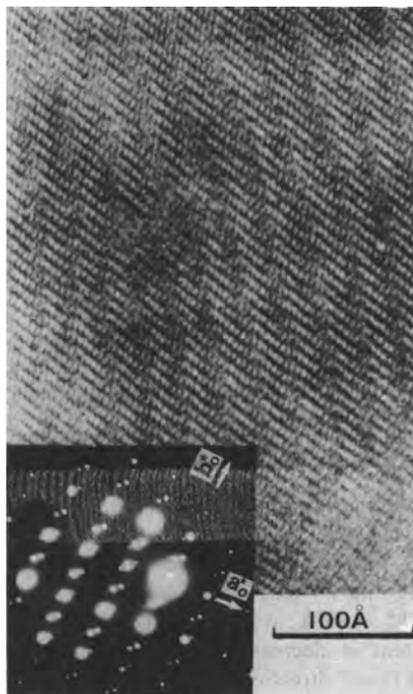


Figure 5 High resolution lattice image of a specimen of labradorite An_{52} and its electron diffraction pattern. The electron beam is parallel to the c_0 axis which is equivalent to [311]. From Nakajima *et al.*²⁴

direction of the lattice vector t joining pairs of e -reflections in the accompanying diffraction pattern. It can be clearly seen that the superlattice arises because of the packing of subcells in an antiphase manner and that the fault vector is $R = \frac{1}{2} [110]$. The absence of c - and d -reflections and the presence of e -reflections symmetrically placed about the positions of b -reflections implies that the superlattice is based on a body-centred ($I\bar{1}$) sublattice. The vector $R = \frac{1}{2} [110]$ is not a lattice vector of the $I\bar{1}$ lattice and antiphase domain boundaries with this fault vector have been observed in specimens of bytownite ($I\bar{1}$ structure, composition A_{77}) and in specimens of synthetic anorthite (An_{100}) which have been cooled through the $C\bar{1} \rightarrow I\bar{1} \rightarrow P\bar{1}$ transitions.¹⁵

⁴⁷ S. H. Chao and W. H. Taylor, *Proc. Roy. Soc.*, 1940, A176, 76.

The first model for the *e*-plagioclase was proposed in 1940 by Chao and Taylor⁴⁷ on the basis of their observation of the *e*-reflections. They suggested a superstructure with alternating slabs of anorthite- and albite-like structures. Although a number of different models have been proposed since then, the latest model of Morimoto and his colleagues^{23,24} based on their TEM observations (as in Figure 5) returns to the original model of Chao and Taylor,⁴⁷ and the later work of Megaw.⁴⁸ Megaw showed that the three-dimensional movement in reciprocal space of the *e*- and *f*-reflections as a function of An-content could be described two-dimensionally by a unit cell defined by the axes a_0 , b_0 , and c_0 , instead of the usual axes of anorthite as follows:

$$\begin{aligned} a_0 &= a \\ b_0 &= \frac{1}{2}a + \frac{1}{2}b \\ c_0 &= \frac{3}{2}a + \frac{1}{2}b + \frac{1}{2}c. \end{aligned}$$

As a starting point, Kitamura and Morimoto²³ assumed that the *e*-reflections lie in the plane of a_0^* and b_0^* and that their positions in that plane move linearly with composition. They also assumed the direction of the *t* vector of An₇₅ and An₂₅ was perpendicular to *a* and *b*, respectively. By using these two vectors, they defined a supercell for *e*-plagioclase as follows:

$$\begin{aligned} a(\text{An}_c) &= ma_0 + n(a_0 - 2b_0) \\ &= ma + n(-b) \\ &= ma(\text{An}_{75}) + na(\text{An}_{25}) \\ b(\text{An}_c) &= 9b_0 = 9/2(a + b) \\ c(\text{An}_c) &= c_0 = (3/2)a + (\frac{1}{2})b + \frac{1}{2}c. \end{aligned}$$

m and *n* are integers with no common divisor, $m/n = (c - 25)/(75 - c)$, and *c* represents the An-content in mol per cent.

By adopting these axes, all the superstructures of the *e*-plagioclases have the same superlattice period along the b_0 axis. The maximum period of the superlattice $T = 1/|t|$ is taken as $9b_0^* = 42 \text{ \AA}$ at An₇₅. The different superstructures which develop as the An-content is decreased to An₂₅, involve the swinging of the superlattice planes about the c_0^* direction, as shown schematically in Figure 6. There is striking agreement between the model for An₅₀ and the electron micrograph shown in Figure 5.

However, in spite of the elegance of this model, it must be accepted with some slight caution in view of the apparent discrepancy between the value of the superlattice period assumed for the ideal model structure at An₇₅ and the much larger periods which have been observed at compositions around An₇₅ (see Background discussion above). Further, the model does not predict any discontinuity in both the magnitude and direction of *t* which Slimming²¹ claims is apparent at compositions around An₅₀.

3 Defects and Microstructures in Microcline and Anorthoclase

At high temperatures the alkali feldspars form a solid solution series of monoclinic structures from monalbite to high sanidine. However, at lower temperatures there is little solid solution and exsolution into K-rich and Na-rich feldspars occurs. The exsolution microstructures which develop in specimens over the composition range

⁴⁸ H. D. Megaw, *Proc. Roy. Soc.*, 1960, A259, 159.