

Local fluctuations in feldspar frameworks

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ABSTRACT

At any set of thermodynamic conditions a mineral will have some well defined equilibrium crystal structure. However, this structure can be locally disturbed by crystal defects, such as domain walls or solute atoms. This distorted structure will only affect a finite volume within the crystal, but the need to retain continuity within the crystal means that this volume must be non-zero. This means, for example, that the boundary between two domains will include a transition zone from one domain's crystal structure to that of the other domain. Thick twin domain walls can be studied quantitatively, by measuring the intensity of diffuse diffraction between pairs of twin-related Bragg peaks. In alkali feldspar (Or₃₀) at room temperature, these walls are approximately 25 Å thick. Similarly, a single solute atom in a mineral will only affect a small region within a crystal. As a result, chemical mixing will only occur in a substitutional solid solution once there is significant overlap between the strain fields around individual solute atoms. This causes the 'plateau effect', where the properties of a phase transition are independent of composition. In alkali feldspar, this plateau extends from albite to 2% Or, which corresponds to a strain field radius of 10 Å.

These phenomena can be modelled using Ginzburg-Landau theory, which predicts that the range of these strain fields will increase as the temperature is raised to T_c . This has been confirmed by measuring the thickness of twin walls as a function of temperature.

KEYWORDS: feldspar, crystal structure, framework, local fluctuations.

Introduction

CRYSTALLOGRAPHY is largely concerned with determining the ideal crystal structures of materials, how they change, and how these structures affect observed crystal properties. The concept of a structure consisting of a lattice and motif emphasises this, and X-ray diffraction gives a time-and-space-average of the sample structure.

Determining the atomic-scale structure of defects is significantly harder. Much of the problem is due to the very small length scale of defects; there is very little material to perform experiments on.

In many cases, these defect structures can be related to the host structure. The key to doing this

is that there is often a requirement to maintain continuity of some feature of the crystal structure between the host and the defect. For example, when pyroxenes exsolve, the SiO₃ chains are largely undisturbed, and maintaining chain continuity constrains the orientation and structure of the augite–pigeonite boundaries.

Feldspar minerals have a framework of aluminosilicate tetrahedra. There is therefore three dimensional continuity to consider. If some small part of a feldspar crystal is distorted by a defect, its structure will blend into that of the bulk. This helps fix the atomic structure at the core of the defect. It leads, however, to another question; what length scale is required for a defect structure to relax back to the bulk equilibrium structure?

Twin domain walls provide a good example of this effect. The first part of this paper shows how Landau theory can give a quantitative description of the form of the fluctuation around a twin. The

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predictions of Landau theory are then compared with experiments, measuring the twin wall by X-ray diffraction.

The same principle — that a locally induced distortion will decay over some finite length scale — also applies to the behaviour of solid solutions. Here, the local distortion results from substituting one atomic species for another. Dilute solid solutions would be expected to deviate from regular solution behaviour, since a few isolated solute atoms are unable to distort the bulk material.

The anorthoclase solid solution was selected as a case study. The reason for this is that disordered alkali feldspar has one displacive transition ($C2/m \leftrightarrow C\bar{1}$); the Al, Si ordering transitions are slow enough to be ignored under most laboratory conditions. The displacive transition is well characterised (e.g. Kroll, 1983; Salje *et al.*, 1985; Zhang *et al.*, 1996, and references therein) and is very nearly second order. The transition temperature varies quite strongly across the solid solution, from *c.* 1250 K for pure albite to room temperature for Or_{34} .

Thickness of twin walls

Introduction

Anorthoclase is characterised by cross-hatch twinning in a general thin section, which appears as lamellar twins in the (010) section shown in Fig. 1. These twins are the result of the monoclinic \rightarrow triclinic phase transition which takes place on cooling. The orientation of the two sets of twin boundaries (albite twins parallel to

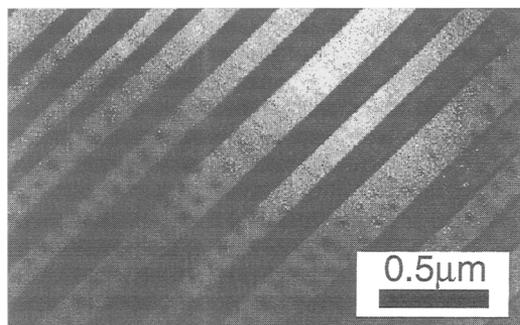


FIG. 1 (010) TEM image of pericline twins in anorthoclase; the pericline twins shown are approximately parallel to (001).

(010) and pericline twins parallel to ($h0l$)) are fixed by the compatibility condition for the structure. These conditions are derived (Eshelby, 1956; Teodosiu, 1982; Landau and Lifshitz, 1986) from the idea that the components of the strain tensor are not independent; there are more components in the strain tensor than there are degrees of freedom for the structural distortion. Mathematically, this is expressed in the equality of certain second spatial derivatives of the displacement field, which is equivalent to the first derivative of the strain field.

If a structure with a twin boundary is modelled in this way, we have two regions with equal and opposite spontaneous strains. Using the compatibility condition, it can be shown that the required equalities are only satisfied for certain twin orientations. This approach is applicable for all ferroelastics. The exact orientations of the twin walls may be further constrained by the point-group symmetry of the strain tensor.

Often this condition reduces to the lattice matching condition; the strain-free boundaries can then be located by considering the geometry of the crystal lattice in the two domains. This is the case for feldspars.

This argument is only part of the story. Although atomic co-ordinates can be made to match up in this way, a totally sharp boundary between the two domains is not likely; it would imply (for example) some extremely unfavourable bond angles. Therefore there must be some kind of gradual transition from one triclinic domain to another. This is illustrated in Fig. 2.

Theory

There is therefore some length scale over which there is a distinct twin wall structure. To develop a theory of what this length scale is, it is useful to consider the geometry of the twin wall in another way. Suppose we were able to insert a thin slice of monoclinic feldspar into a triclinic bulk. To get any sort of match at all, the monoclinic slice must be suitably oriented. The triclinic material closest to the monoclinic slab will be slightly distorted — it will be closer to being monoclinic than the rest of the sample. The length scale of the distorted region will be a balance between the energy of not having the equilibrium degree of triclinicity, and the energy required to bend the structure.

The resulting structure would look exactly like a twin wall. Indeed, by definition the middle of the triclinic (+) \rightarrow triclinic (–) boundary must be

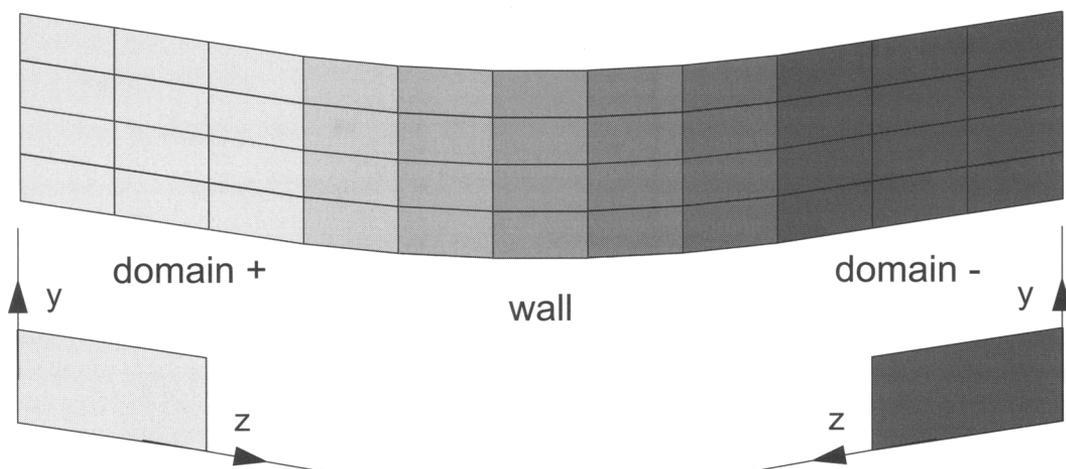


FIG. 2. Schematic unit cell-scale structure of a pericline twin and wall.

monoclinic. So the thickness of a twin wall will be driven by the same two forces.

Quantitatively, this behaviour can be described by the Ginzburg-Landau model (Salje, 1990). If the displacive order parameter Q (in the case of anorthoclase, this is the degree of triclinicity, given by $\cos \alpha$ or $\cos \alpha^*$) varies as a function of position x , then the energy of the structure is given by

$$\begin{aligned}
 G &= \int G(x) dx \\
 &= \int \frac{1}{2} A(T - T_c) Q^2 + \frac{1}{4} B Q^4 + \dots \\
 &\quad + \frac{1}{2} g (\nabla Q)^2 + \dots dx
 \end{aligned} \quad (1)$$

and so the equilibrium structure for $Q(x)$ will be the one that minimises G . The absolute lowest energy comes from having $Q = Q_0$ across the entire structure — in other words, having the whole crystal in a uniform equilibrium structure. However, if the boundary condition that $Q = 0$ (i.e. monoclinic) at $x = 0$ is added, then the structure around that point is given by

$$\begin{aligned}
 Q &= Q_0 \tanh \left(\frac{x}{w} \right) \\
 w &= \sqrt{\frac{2g}{A(T_c - T)}}
 \end{aligned} \quad (2)$$

The length scale of the twin wall is given by the halfwidth w , which increases as the temperature

increases towards the transition temperature. The excess energy of the monoclinic slab gets smaller as T_c is approached. Since the bending energy does not vary with temperature, the bending term becomes the dominant one in equation (1). This drives the increasing wall thickness.

Diffraction experiments

Measuring the wall thickness is more easily done in reciprocal space (i.e. using diffraction methods) than in real space (i.e. HRTEM). The main reason for this is that the difference between the two domain orientations is quite subtle—of the order of 5° . As a result, it is not easy to determine the twin profile with enough precision to fit the wall width well.

In the diffraction pattern of a twinned material each reciprocal lattice point is split into a number of spots, corresponding to the number of distinct twin domains. These spots are connected by much weaker streaks. The whole pattern (the spots and the streaks) corresponds to the Fourier transform of the structure shown in Fig. 2. These weak diffraction effects can be seen quite easily in an electron diffraction image, such as Fig. 3. This confirms that domain walls exist, but since intensity data cannot be extracted from this technique, electron diffraction does not allow us to determine the wall thickness.

Quantitative information can be obtained from X-ray diffraction. This is experimentally challenging, since the diffraction signal being studied is

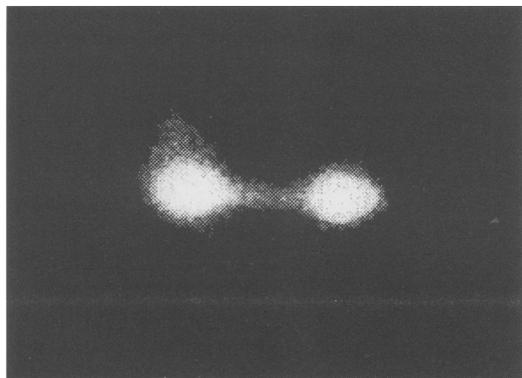


FIG. 3. Enlargement of 006 peak in the $a^* : c^*$ reciprocal lattice section of twinned anorthoclase.

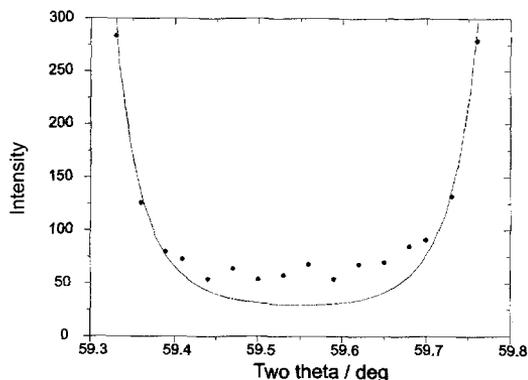


FIG. 4. Twin wall diffraction signal, measured by XRD. The main Bragg peaks are of the order of 3000 counts each.

very weak; typically, the wall signal is around 1000 times less intense than the Bragg peak. Suitable XRD apparatus (Salje, 1995; Locherer *et al.*, 1996) uses multichannel (linear or area) detectors to maximise the counting efficiency. Hayward *et al.* (1996) used this technique to study pericline twin walls in anorthoclase.

Figure 4 shows the wall signal as the excess intensity between two Bragg peaks. The ratio of excess intensity to Bragg intensity depends on the volume fraction of (distorted) twin wall to undistorted bulk. Given the twin density, which can be measured from TEM images, the thickness of the individual twin walls can be determined. The temperature dependence of the wall thickness is shown in Fig. 5, together with a fit based on the Ginzburg-Landau model in equations (1) and (2).

Significance of twin walls

The volume occupied by the twin walls as a fraction of the total material is small — only a few percent. As a result of this, many bulk properties — for example, the heat capacity or compressibility — are not greatly affected by the presence of twin walls. For example, the energy associated with the twin walls can be determined by integrating equation (1) across the wall profile. If the twins are 1500 Å apart, the twin wall energy is about 2% of the energy released by the monoclinic–triclinic phase transition.

Properties which will be modified by the behaviour of the twin walls are those which are essentially localised. This is the case for the

solubility of defects and trace elements, and for diffusion properties.

Crystal defects, which include solute atoms, will be more stable along domain walls than in the bulk. The reason for this is that since the wall is a defect structure anyway, the energy cost for another defect also being at that site will be smaller.

This mechanism has been used to explain the twin memory behaviour seen in ferroelastics such as the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Voronkova and Wolf, 1993). Defects collect along the twin walls in the low symmetry phase. If this material is then heated above its transition temperature, the domain walls vanish, but the lines of defects remain. On cooling, these lines are the best sites

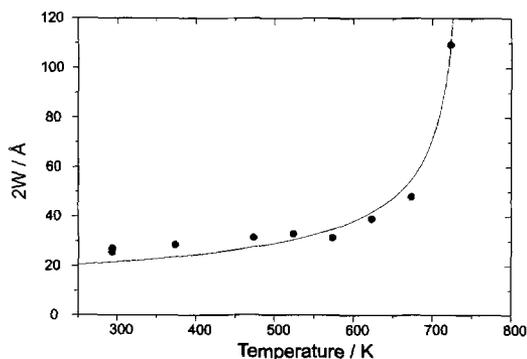


FIG. 5. Temperature dependence of twin wall thickness. The transition temperature for this sample is 733K.

to reform the domain boundaries. Thus, if a material is briefly heated above its transition temperature then cooled again, the twin structures before and after heating will be identical.

In the case of potassium in albite, there is another force which should drive the collection of K along the twin walls. Since the centre of the twin wall is locally monoclinic, K atoms will be more stable there than in the triclinic bulk. This implies that there is a major compositional difference between the twin walls and the bulk. Experiments to try to measure this effect are underway.

Transport properties may also be enhanced by the presence and extent of twin walls. Yund *et al.* (1981, 1989) studied the effect of dislocation pipes on oxygen and cation diffusion in feldspar. Twin walls are, if anything, even more extended, and should also enhance diffusion coefficients. However, under most petrologically relevant

conditions, intrinsic (bulk) diffusion is the dominant diffusion mechanism. A possible exception to this is (Al,Si) interdiffusion. This is normally so slow that any enhancement should be significant. The fact that twin walls are locally monoclinic (so equal occupancies of Al and Si on T_{1c} and T_{1m} are expected) should also make (Al,Si) diffusion easier.

The plateau effect in a solid solution

Introduction

The finite thickness of twin walls is the result of attempting to include a locally monoclinic region in a triclinic bulk. Similar local distortions can be generated by changing chemical composition across the analbite-sanidine solid solution. This is summarised schematically in Fig. 6. Sodium feldspar is triclinic at room temperature, because the crankshaft framework collapses around the

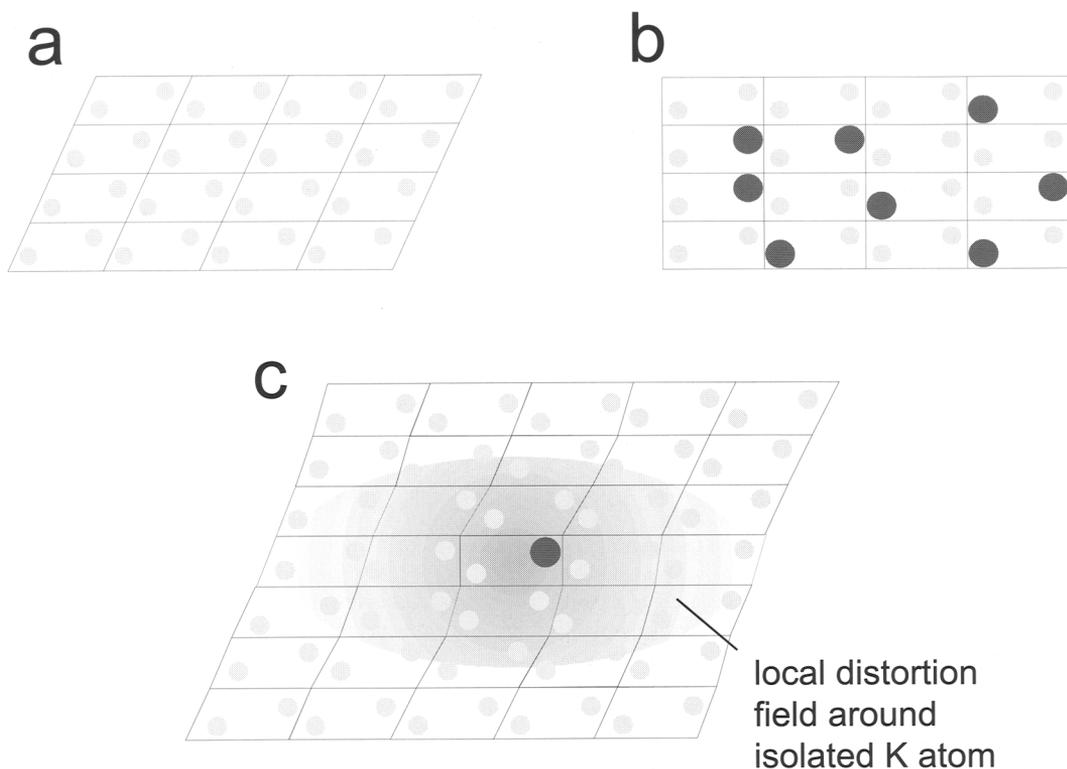


FIG. 6. (a) and (b) Schematic representation of regular solution behaviour; pure analbite is triclinic at room temperature, K rich anorthoclase is monoclinic. (c) Schematic behaviour of dilute solid solution. The isolated K atom is only able to distort a finite neighbouring region.

small Na cations. By substituting larger K for Na, the degree of collapse is reduced until, at around $\text{Ab}_{66}\text{Or}_{34}$, the monoclinic structure is stable at room temperature.

Implicit in this approach is the idea that the effect of $\text{K} \leftrightarrow \text{Na}$ substitution is additive — twice the K content has twice the stabilising effect. This is the regular solution model, which also implies that the (Na,K) distribution, and the resulting strain field, are homogeneous.

For dilute solid solutions, a different mechanism can be imagined, originally suggested by Ilyama and Volfinger (1976) and Newton and Wood (1980). Placing a single K atom on a single Na site will cause the structure in the immediate vicinity to be monoclinic, rather than triclinic. Around this, there will be a halo of distorted material, analogous to the wall around a twin. Beyond this, the distortion caused by the K atom will be minimal.

The local fluctuation model therefore predicts a plateau in the temperature-composition phase diagram for the $C2/m \leftrightarrow C\bar{1}$ displacive phase transition in anorthoclase. For samples with a reasonably large amount of K, the transition temperature will be linear with composition, but in K poor samples, the transition temperature will be independent of composition. The extent of this plateau will depend on the spatial extent of the halo around each isolated K atom.

Experimental observation of the plateau effect

Hayward and Salje (1996) synthesised a suite of anorthoclases in the composition range Ab_{100} to $\text{Ab}_{92}\text{Or}_8$. The monoclinic \leftrightarrow triclinic transition temperature was determined for each of these samples using X-ray diffraction. The resulting phase diagram, which shows a plateau at approximately $\text{Ab}_{98}\text{Or}_2$, is shown in Fig. 7.

It is significant that the transition temperature is less well determined at the edge of the plateau. At these compositions, the distortion fields around individual K atoms are just beginning to overlap. The degree of overlap, and the extent to which the K atoms stabilise the bulk increases with temperature, since the halo around each K atom expands with heating.

From the composition range which shows plateau behaviour, it is possible to estimate the radius of the distortion caused by the individual atoms. If the atoms are randomly distributed, the halo radius is 10 \AA , which is somewhat less than the halfwidth of the twin walls at room

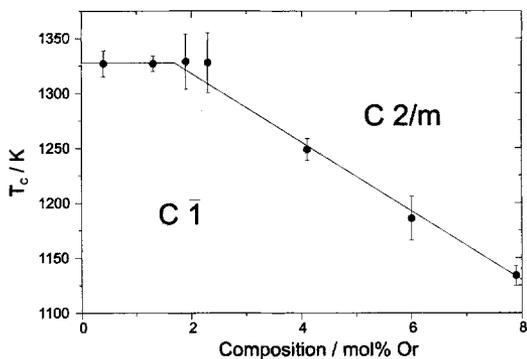


FIG. 7. Albite-rich end of the anorthoclase phase diagram.

temperature. However, there is probably a degree of clustering of K atoms. In particular, K atoms would be expected to collect on domain boundaries in the samples. If K atoms are clustered in this way, the radius of the distortion around each K atom must be somewhat larger than the estimate above.

Further examples of local fluctuations

Both these examples have involved distorting a local region in a feldspar crystal — a fraction of a unit cell — and determining how far away the effect of this distortion can be observed. There are a number of other mechanisms which produce local distortions, and which may be expected to behave in a similar way.

The relaxations which occur at grain surfaces occur because the top layer of a crystal structure is only held in place from below, and not from above. This radically changes the material properties compared with the bulk. In the case of feldspar, the surface relaxation penetrates around 20 \AA into the crystal at a temperature near T_c (Harrison and Salje, 1994), which is comparable with the results obtained here.

Incommensurate structures are also modulated on a local scale. In general, the wavelength of the modulation is fixed by the point in reciprocal space where the component structures are able to interact (Heine and McConnell, 1981, 1984). However, there is a minimum wavelength that is possible, which is constrained by how sharply the structure can be bent. In the plagioclase solid solution, the shortest modulation wavelength reported is 17 \AA (Slimming, 1976) for a sample $\text{Ab}_{65}\text{An}_{34}\text{Or}_1$.

The local fluctuations described so far have all been static phenomena, observed below the transition temperature. There is evidence from both spectroscopic studies and computer modelling that thermal fluctuations exist above T_C . In the case of anorthoclase, this would take the form of short-range, short-lived patches of triclinic material in the monoclinic bulk. Individual fluctuations do not exist for long. Also, they are only locally correlated; individual thermal fluctuations are independent of each other. As a result, the time-and-space average structure (which is what diffraction experiments generally measure) remains monoclinic.

The behaviour of static fluctuations allows us to speculate about the structure of these fluctuating patches. The principle is that if one unit of the structure — say the motif around one lattice point — changes its structure in some way, its neighbours must respond. This response consists of a similar, but attenuated, change. A single structural unit cannot change in isolation. By analogy with (for example) the behaviour of the analbite structure around a single K atom, we might expect the size of one of these patches in real space to be of the order of tens of Ångströms.

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