Computer simulation of a microstructure in a potassium feldspar

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Abstract

Kinetics of atomic ordering in a potassium feldspar is simulated using massively parallel computing. The simulation method is based on the Monte Carlo algorithm for the Al-Si redistribution (the Kawasaki dynamics) combined with the lattice relaxation. The Hamiltonian has the symbolic form

$$H = \frac{1}{2}uAu - uFp$$

where u represents displacements of atoms from ideal positions, and p the Al and Si occupation numbers. The model is purely elastic; there is no direct interaction between Al and Si atoms. The simulated crystal is a thin film with (010) surfaces and consists of 64×64 unit cells; the unit cell defined for the whole film contains slightly more than 4 formula units. The (010) orientation is chosen in order to preserve in the film the main structural feature of feldspars: crankshaft-like sheets formed by four-tetrahedra rings. This makes it possible to observe the Pericline twins only. At the late stage of the kinetic run these twins are clearly seen. The direction for the domain walls is determined by the spontaneous strain and changes with the change of the model parameters; considerable local deviations from this direction are observed.

KEYWORDS: feldspar, microstructure, phase transition, kinetics, domains.

Introduction

THE crystal structure of potassium feldspar, $KAlSi_3O_8$ (MT_4O_8), is envisaged as a three-dimensional framework of corner-sharing AlO_4 and SiO_4 tetrahedra, with potassium atoms occupying large framework cavities. The basic elements of this framework are four-tetrahedra rings; such rings form crankshaft-like sheets perpendicular to the (010) direction. A tetrahedron containing an Al atom is somewhat larger than the equivalent Si tetrahedron; mean Si–O and Al–O bond lengths are 1.62 Å and 1.75 Å, respectively (e.g. Smith and Brown, 1988; Putnis, 1992). This difference in the size between the two types of tetrahedra is accommodated within the framework by some local deformation. We now consider the Al/Si ordering transition $C2/m \rightarrow C\bar{1}$.

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The driving force of this transition is the interaction between Al and Si atoms; in particular, there is a resulting repulsion between two Al atoms occupying neighboring tetrahedra. This circumstance is frequently formulated in terms of the so-called Al avoidance rule: two Al tetrahedra usually do not share a corner if the Si:Al ratio is greater than one (e.g. Megaw, 1973).

Below the transition, potassium feldspar has a characteristic twin microstructure with two types of twins (Albite and Pericline) observed (Brown and Parsons, 1994). The spontaneous strain tensor has non-zero ε_{xy} and ε_{yz} components, and possible orientations of domain boundaries can be determined from the requirement that the atomic displacements in the domain-wall plane must be identical for both adjacent domains. This requirement is expressed mathematically as the compatibility condition (Sapriel, 1975):

$$\sum_{ij}\left(\varepsilon_{ij} - \varepsilon'_{ij}\right)x_i x_j = 0 \qquad (1)$$

where ε_{ij} and ε'_{ij} denote components of spontaneous strain tensors for two domains, and x_i is a coordinate of a point in the domain-boundary plane. In the case under consideration $\varepsilon_{ij} = -\varepsilon'_{ij}$ and Eq. 1 has two solutions: (i) $y = 0$ (Albite twin law) and (ii) $z = -(\varepsilon_{xy}/\varepsilon_{yz})x$ (Pericline twin law) (Salje et al., 1985). The first defines a (010) domain wall; the second corresponds to the domain boundary orthogonal to the (010) plane, with an orientation that is not fixed and depends on the value of the spontaneous strain.

The aim of the present paper is to address a question of the formation and temporal evolution of the microstructure. We report here preliminary results of a computer-simulation study of this problem. In the computer experiment the simulated sample is instantly cooled down across the transition temperature. Different aspects and problems of such simulation are discussed.

The model

The model considered in this paper is an extension of earlier work (Salje and Parlinski, 1991; Salje, 1992; Parlinski et al., 1993a,b; Bratkovsky et al., 1994a,b,c). In this model we distinguish between two groups of sublattices; ordering takes place on the sublattices of the first group, while the second group is not involved in the ordering process. The sublattices of the second group form the host lattice Ordering atoms interact with the host lattice producing static distortions (i.e. shifting the equilibrium positions of the host atoms). In the model this ability of the ordering atoms to distort the host lattice is described by the so-called Kanzaki forces (Khachaturyan, 1983) with which the ordering atom acts on neighbouring host atoms at the sites of the unperturbed host lattice. Thermal displacements of the host atoms (vibrations around shifted equilibrium positions) are not taken into account.

When a system consists of two interacting subsystems, its Hamiltonian contains three terms: the first two are the Hamiltonians of the subsystems themselves and the last is the interaction term. In the present case the Ilamiltonian is

$$H = H_{host} + H_{ordering} + H_{interaction} \qquad (2)$$

Here the first term is a potential energy of the host lattice in a harmonic approximation; for the second term it is assumed that there are no direct interactions between the ordering atoms and, therefore, $H_{ordering} = 0$. The last term describes the above-mentioned interaction between the ordering atoms and those of the host lattice. The explicit expression for the Hamiltonian (2) is

$$H = \frac{1}{2}uAu - uFp \qquad (3)$$

$$= \frac{1}{2}\sum_{nm}\sum_{ij}u_n^i A_{nm}^{ij}u_m^j - \sum_{nl}\sum_i\sum_s u_n^i F_{nl}^{is}p_l^s \qquad (4)$$

In Eq. 3 matrix notation is used. Here u denotes the displacements of the host toms from the ideal positions, A is the Born-von Karman tensor of the host lattice, F is the set of the Kanzaki forces and p represents the occupation numbers for the ordering atoms; n,m,l are the cell+sublattice indices, i,j the Cartesian indices, and s is the ordering-atom type index. Such Hamiltonians arise naturally as a result of an expansion of the internal energy of the system in powers of the small static displacements of the host atoms (Krivoglaz, 1969; Khachaturyan, 1983).

In the case of potassium feldspar we assume that the size of a tetrahedron in the undistorted host lattice corresponds to that of the Si atom inside. It means that the Si atom does not produce any distortion, and the corresponding forces are zero. The difference in size between AlO_4 and SiO_4 tetrahedra is simulated by central repulsive forces by which the Al atom at the centre of the unperturbed tetrahedron acts on the oxygen atoms at its vertices producing the expansion of the tetrahedron. The host lattice has then to accommodate the resulting mixture of tetrahedra of two different sizes. We also need to specify the Born-von Karman tensor A in the Eq. 3, in other words, the character of interatomic bonds constituting the host lattice. Several types of the bonds are taken into account: (i) intra-tetrahedron $O-O$ bonds providing the elastic response of a tetrahedron to the Kanzaki forces; (ii) $M-O$ bonds responsible for the stability of the structure; (iii) $M-M$ bonds forming a lattice of hexagons in a mirror plane; (iv) inter-tetrahedron bonds which connect oxygen atoms belonging to neighbouring tetrahedra. The bonds of the last type are necessary for the elastic repulsion of two Al atoms occupying neighbouring tetrahedra (the Al avoidance rule), and also for preserving the $T-O-T$ bond angle. The latter is often achieved by introducing an extra 'bond-bending' term into the Hamiltonian (see, for instance, Catlow, 1988).

The simulation

To change the distribution of ordering atoms in the simulated sample, we use the Monte Carlo method and the Kawasaki dynamics (see, e.g. Binder and Stauffer, 1987), interchanging atoms of corner-sharing tetrahedra. An approximation similar to the adiabatic approximation is adopted; we assume that the host lattice immediately reaches the equilibrium corresponding to a new configuration. This approximation is certainly valid since characteristic phonon

times are much smaller than the time interval between two successive attempts to change the distribution of ordering atoms. Thus each successful change is always followed by a complete relaxation of the host lattice. As is seen from the Eq. 3, the static displacements of the host atoms are

$$u^{eq} = A^{-1}Fp \qquad (5)$$

Such a calculation would mean an inversion of a very large, sparse matrix A. Instead, the equation of motion for atomic displacements is solved numerically. Two equations are used in the simulation to calculate lattice relaxation: (i) equation for motion with energy dissipation (friction),

$$m\, d^2u/dt^2 + \gamma\, du/dt = f \qquad (6)$$

where m is the atomic mass, γ the friction coefficient, f the external force, and (ii) equation for motion with constant velocity when external and friction forces compensate each other exactly,

$$du/dt = f \qquad (7)$$

The Eq. 7 is a particular case of Eq. 6 ($d^2u/dt^2 = 0$, $\gamma = 1$) and corresponds to purely relaxational dynamics. Here the external force f is the sum of the Kanzaki force F and the reaction force of the deformed host lattice. As t goes to infinity, the atomic displacements approach their equilibrium values (5). For the numerical solution of the Eqs. 6 and 7, we use the method of molecular dynamics (Dove, 1988) and the Euler method (Press et al., 1986), respectively.

Such kind of simulation is essentially beyond the capabilities of computers with ordinary architecture and needs parallel computing. The computer code for the simulation is written for the massively parallel computer AMT DAP 610 which is a peripheral processor attached to a host computer. It is a SIMD (single instruction, multiple data) device in which processor elements act on individual data sets but with a common instruction stream that is broadcast from a central processor. The processor elements are arranged in a square 64×64 matrix. This geometry makes it reasonable to simulate a sample consisting of $n_1 \times n_2 \times n_3$ unit cells, where $n_1 = n_2 = 64$. In this case all information about n_3 unit cells is put into one processor element. The number of unit cells in the third direction remains arbitrary, but is limited by the speed of calculation and the degree of complexity of the unit cell. Usually the reasonable value of n_3 is much less than 64, and the shape of the simulated specimen is necessarily that of a slab.

In the case of potassium feldspar the structure of the unit cell is quite complicated. Because of this the simulated sample has the form of a very thin film; the computational 'unit cell' defined for the whole film contains slightly more than four formula units

(Fig. 1). The film has (010) orientation, which is chosen in order to preserve in the sample the main structural feature of feldspars, the crankshaft-like sheets made up from four-tetrahedra rings, and the film contains two crankshafts. This makes it possible to observe the Pericline walls only. Free boundary conditions are used. Finally, the undistorted host lattice is somewhat idealized in comparison with the real sanidine structure; see Fig. 1. In reality there is some additional rotation of the tetrahedra. This difference in structure leads, for example, to the $120°$ value of the β angle, instead of the experimentally observed value $\beta = 116°$ (Megaw, 1973).

The most serious problem in simulating a system with lattice-mediated interactions is the calculation of the energy difference between two configurations of ordering atoms. This quantity is of primary importance for the Metropolis algorithm, since it determines whether a new configuration is accepted or rejected. In the case of the Kawasaki dynamics one has to take an initial distribution of ordering atoms, relax the host lattice according to this configuration, calculate the total energy of the system, then exchange one pair of atoms, relax the host lattice again, calculate the new total energy and, finally, the energy difference. The difficulty here is that this calculation would be far too slow since (i) it involves two lattice relaxations per exchange attempt and (ii) it is impossible to use this algorithm for parallel computation. It would be desirable to select as many non-overlapping pairs of ordering atoms as possible (ideally, covering all the crystal) and make all exchange attempts independently after having relaxed the host lattice only once. The simplest idea which emerges is to calculate the energy difference in exchanging a pair of ordering atoms without subsequent lattice relaxation. This procedure is much faster and does allow parallelization; however, it is obviously incorrect. Nevertheless, it turns out to be possible to correct the result afterwards, as explained below.

Thus, we would like to exchange ordering atoms and compare energies of two configurations, both of which are in the effective field of the host lattice relaxed according to the old configuration. Surprisingly, it can be shown that for the case under study (the Kawasaki dynamics and zero Kanzaki forces for one sort of ordering atoms) the energy difference calculated this way is connected with the correct one by a simple equation

$$\Delta E_{nm}^{correct} = \Delta E_{nm}^{incorrect} + 2E_n + 2E_m - E_{nm} \qquad (8)$$

where E_n and E_{nm} are the energies of a single atom (at site n) and a pair of atoms (at sites n and m) in the otherwise empty host lattice, respectively. In the infinite sample these quantities are the same for each
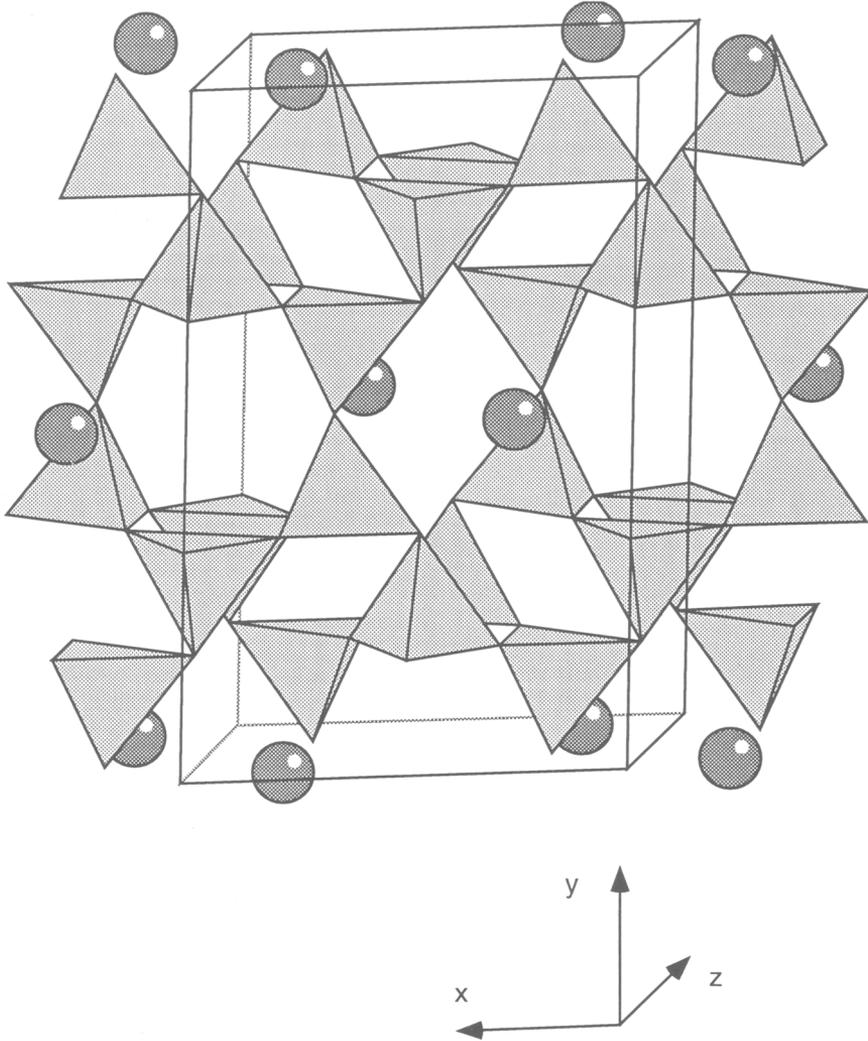
FIG. 1. The unit cell of the simulated thin film of the potassium feldspar defined with respect to the whole film. The simulated sample is obtained by the translation of this cell in x and z directions. All the tetrahedra are of the same size and correspond to the host lattice before applying the Kanzaki forces. Spheres represent potassium atoms.

unit cell and depend only on the sublattice indices. This means that it is possible to calculate all these necessary energies once in advance and then use them for the energy-difference correction. In the case of a finite sample the above energies have certain spatial variation close to the sample surfaces; however, in the simulation presented here we ignore this variation and calculate these energies for one of the central unit cells.

The existence of a free surface in a sample undergoing the order-disorder phase transition always means some degree of surface segregation (e.g. Zangwill, 1988). The concentration of each sort of atom becomes a function of a layer index. The closer the atomic layer is to the surface, the greater is the deviation of the concentration from the bulk value. This effect is especially important for a thin film. In the case considered here, it is energetically favourable for the Al atoms to concentrate at the (010) surface of the feldspar film. The distortion of the host lattice produced by the Kanzaki forces is minimized this way. In order to prevent this
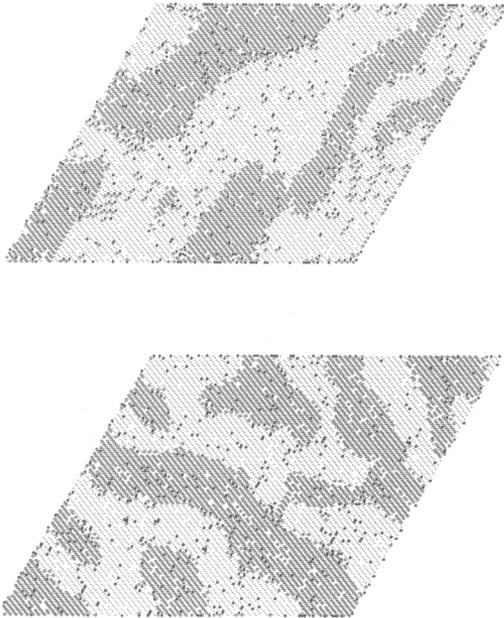
FIG. 2. The distribution of Al atoms over the tetrahedral sites belonging to one of the crankshafts, after 600 Monte Carlo steps per atom, for two different sets of the parameters of the host lattice. In these two cases, domain walls have distinctly different preferred orientations, demonstrating the dependence of domain wall orientation on the choice of model parameters. Different symbols are used to show Al atoms at sites allowed for two possible variants of the ordered phase (dots and open circles) and those at other sites (filled circles).

segregation and mimic the properties of bulk potassium feldspar crystal, we slightly increase strengths of the intra-tetrahedron bonds at the (010) surfaces. The criterion is the natural requirement of equality of the energies of a single Al atom at the surface and in the crystallographically equivalent layer inside the film. This leads to about 10% increase of the spring constants of the surface intra-tetrahedron bonds.

Results and discussion

In our study of the kinetics of microstructure formation in the simulated potassium feldspar, the specimen is initially in equilibrium at some temperature above the transition; the Al$-$Si distribution is disordered (in fact, in the kinetic runs discussed here we start from a completely random Al$-$Si distribution, i.e. from the equilibrium config-

uration at infinite temperature). Then the sample is instantly cooled down across the transition, in other words, the temperature rapidly decreases to the value which corresponds to the ordered phase in equilibrium. The aim is to observe the process of transition from sanidine to microcline.

At the early stage of the kinetic process, fine patches of two ordering variants of microcline (corresponding to two possibilities of ordering Al atoms on T_1 sites) arise, and the soft direction for the Pericline domain walls is sometimes barely perceptible. Then the patches start to coarsen, and the soft direction gradually begins to emerge. At a later stage, we observe sufficiently wide stripes of the Pericline twins; evolution of the sample at this stage is very slow, which precludes further development of the stripe pattern. Even after the stripes have been formed, considerable local deviations of the domain walls from the soft direction are observed; this observation is in agreement with the experimental findings. The overall direction for the domain walls changes with the change of model parameters, as might be expected from the solution of the compatibility equation (1) for potassium feldspar, since the spontaneous strain in the ordered phase is also sensitive to the choice of model parameters. The microstructure at this stage for the two sets of model parameters is shown in Fig. 2. Different soft directions are clearly seen. Only the Al atoms are indicated; different symbols are used to show Al atoms at sites legal for two ordering variants of microcline and Al 'impurity' atoms (at sites different from T_1).

The study reported here is the first step towards the general goal to simulate bulk properties of feldspars on a mesoscopic length scale. In order to separate clearly surface and finite-size effects from the bulk kinetics, it is necessary to simulate, first of all, thicker samples and then to increase their size in x and z directions. It is important also to consider different orientations of the film (or slab). With this in mind, considerable attention was paid to the problem of the simulation speed. As a result, the simulation is rather fast, and in the case of the sample considered in this paper is about 200 Monte Carlo steps per ordering atom per hour. This allows us to simulate in the future from 10 to 20 crankshafts in a reasonable time. This work is now in progress.

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