Time-dependent Landau theory for order/disorder processes in minerals

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Abstract

Recent advances in the use of time-dependent order parameter theory to describe the kinetics of order/disorder transitions are reviewed. The time dependence of a macroscopic order parameter, Q, follows, to a good approximation:

$$\frac{dQ}{dt} = -\frac{\gamma\langle a^2\rangle}{2RT}\left[1 - \frac{\xi_C^2}{\xi^2}\exp\left(-\frac{\xi^2}{2}\nabla^2\right)\right]\frac{\partial G}{\partial Q}$$

For systems in which the order parameter has a long correlation length (large ξ) and is not conserved (small ξ_C), the Ginzburg–Landau equation provides a general kinetic solution:

$$\frac{dQ}{dt} = -\frac{\gamma\langle a^2\rangle}{2RT}\frac{\partial G}{\partial Q}$$

Specific rate laws can be derived from this general solution depending on whether the crystals remain homogeneous with respect to the order parameter, Q. The advantages of the overall approach are, firstly, that it does not depend on the detailed structure of the material being examined; secondly, that the order parameter can be followed experimentally through its relationship with other properties, such as spontaneous strain, excess entropy, intensities of superlattice reflections, etc.; and, finally, that conventional Landau expansions in Q may be used to describe the thermodynamic driving forces.

For a simple second-order transition in crystals which remain homogeneous in Q the rate law is:

$$t - t_0 = \int_{Q_0}^{Q} \frac{-2RT}{\gamma\lambda\exp(-\Delta G^*/RT)}\left(\frac{1}{a(T - T_C)Q + bQ^3}\right)dQ$$

If the free energy of activation varies with the state of order of the crystal, this becomes:

$$t - t_0 = \int_{Q_0}^{Q} \frac{-2RT}{\gamma\lambda\exp(-\Delta G^*/RT)}\left(\frac{\exp(\varepsilon Q^2/RT)}{a(T - T_C)Q + bQ^3}\right)dQ$$

Simplifying assumptions can be introduced into the mathematics, or the integrals can be solved numerically. For crystals which remain homogeneous, the simplest solution valid only over small deviations from equilibrium is:

$$\ln(Q - Q_{eq}) \propto t$$

For crystals which develop heterogeneities in Q, the rate laws change significantly and we find as an extreme case:

$$Q^2 \propto ART\ln t + B\frac{\Delta H^*}{RT}$$

where the A coefficient may be temperature dependent.

Experimental data available for a limited number of minerals (omphacite, anorthite, albite, cordierite and nepheline) are used to demonstrate the practical implications of the overall approach. As

anticipated from the theory, modulated structures commonly develop during kinetic experiments, the observed rate laws depend on whether the critical point of the ordering is located at the centre or boundary of the Brillouin zone, and the rate laws for ordering and disordering can be quite different. The importance of different length scales, not only in the different techniques for characterizing states of order (IR, NMR, calorimetry, X-ray diffraction, etc.) but also for interpreting observed mechanisms and rate laws, is also outlined.

Use of the order parameter in Landau expansions and in Ginzburg–Landau rate laws provides, in principle, a means of predicting the equilibrium and non-equilibrium evolution of minerals in nature.

Introduction

THE application of classical equilibrium thermodynamics has proved to be highly effective in calibrating the stability ranges of different mineral assemblages in nature. It is widely recognized, however, that many of the processes involved in the crystallization and sub-solidus evolution of rocks occur under non-equilibrium conditions, and that the constraints of kinetics are not nearly so well defined. These observations reflect the general experience of petrologists that the factors which determine non-equilibrium pathways tend to be diverse and elusive in comparison with the straight minimization of free energy that determines equilibrium. There is, therefore, a real need for general thermodynamic and kinetic theories which depend upon the same key parameters to establish links between equilibrium and non-equilibrium behaviour. The purpose of the present paper is to outline a new approach to the kinetics of structural phase transitions in minerals which goes some way towards fulfilling this need. We review some recent developments in the application of Landau theory and the associated Ginzburg–Landau kinetic theory and then demonstrate that these ideas have practical implications for the treatment of cation ordering transitions. Fundamental to the whole approach is the use of a macroscopic order parameter, Q, to measure the progress of phase transitions as a function of both time and temperature.

The paper is divided into four sections. In the first section, the basic ideas of time-dependent order parameter theory are introduced. Rather than presenting the full mathematical basis of the master equation, emphasis is placed on qualitative aspects of the approach and the physical insights which the resulting macroscopic rate laws can provide. In the second section, alternative rate laws derived from the Cahn continuum equation and the Ginzburg–Landau equation are compared. Again, the intention is to summarize and amplify experimentally verifiable aspects of formal theory which is presented elsewhere. The origin of 'kinetic' modulated structures is briefly reviewed and, finally, the proposed rate laws are tested for a number of minerals for which kinetic data are available. The specific examples are of Al/Si ordering and disordering in feldspars and cordierite, Na/Ca/Mg/Al disordering in omphacite and the decay of the incommensurate structure of nepheline. Readers who are not familiar with the concepts of Landau theory, or of order parameter theory in general, may wish to read the experimental section first in order to get a feel for the practical direction of the whole approach.

Time-dependent order parameter theory

General background. A crystal in an unstable or metastable state will tend to lower its free energy by undergoing structural changes. Its final equilibrium state is at some minimum in free energy, whereas the rate at which it approaches this minimum is determined by the particular pathway it follows. For any set of external variables (P, T, etc.) there is only one true minimum in the free energy but there may be an infinite number of possible reaction pathways. Not surprisingly, the problem of predicting which pathway will actually be followed, and hence of defining the probable rate of transformation, may be more complex than merely characterizing the equilibrium state.

In order to identify the most probable pathway for a phase transition in a crystal it is first necessary to examine the statistics of structural changes, or steps on a microscopic scale, within that crystal. The most probable of these microscopic steps will, of course, determine the direction of change on a macroscopic level and it is then necessary only to sum the individual steps according to their assigned probabilities. Glauber (1963), Metiu *et al.* (1976a,b) and Salje (1988a) have shown that, by a judicious selection of parameters, kinetic expressions which describe the time-dependence of the order parameter, Q, for the transition can be obtained. Since Q may be the same order parameter as used in Landau free energy expansions, the rate laws effectively chart the passage of a system over a well-defined free energy surface

towards the minimum point. The close relationship between kinetic and equilibrium behaviour is thus established through the use of a macroscopic parameter which can, in turn, be related to other experimentally accessible macroscopic parameters, such as spontaneous strain, excess entropy and enthalpy, birefringence, intensities of superlattice reflections, etc.

Mathematical background. The starting point for time-dependent order parameter theory is a Markovian master equation. Over a given small volume of a crystal there is a probability, P, that some physical parameter will have the value n at time t. This probability will change with time according to the statistics of small changes, of magnitude a, occurring in the value of the local parameter n as:

$$\frac{1}{\gamma} \cdot \frac{\partial P(n,t)}{\partial t} = - \sum_a W(n \rightarrow n + a) P(n,t) + \sum_a W(n - a \rightarrow n) P(n - a,t) \quad (1)$$

(Glauber, 1963; Metiu *et al.*, 1976*a,b*; Salje, 1988*a*). $W(n \rightarrow n + a)$ is the probability that the local parameter will jump from n to $n + a$ in a unit of time given by $1/\gamma$, where γ is a characteristic frequency of the system. $W(n - a \rightarrow n)$ is the probability for the reverse, jump, etc. It is then assumed that the jump probabilities follow Boltzmann statistics and that the most probable macroscopic pathway is given by integration of the most probable microscopic steps along the reaction pathway. In the macroscopic solution given by Salje (1988*a*), after Metiu *et al.* (1976*a,b*), Q is eventually identified with n giving:

$$\frac{dQ}{dt} = \frac{-\gamma \langle a^2 \rangle}{2RT} \left[1 - \exp\left(\frac{\xi^2}{2} \nabla^2\right) \right] \frac{\partial G}{\partial Q} \quad (2)$$

where R is the gas constant and ∇ is the gradient operator. The term $\langle a^2 \rangle$ is a correlation function which should be regarded as a material constant. The original physical significance of the a parameter is lost in the integration procedure but, since it is related to the jump size for a given unit of time, it can be used to account for the temperature dependence of individual steps. The size of jump in a fixed time at high temperatures will be greater than at low temperatures for an activated state model. Thus:

$$\langle a^2 \rangle = \lambda \exp(-\Delta G^*/RT) \quad (3)$$

where λ is a material constant and ΔG^* is the free energy of activation.

The term ξ is introduced in the statistical analysis in order to define the extent to which individual steps in the order parameter locally in a crystal will influence or induce changes in the same parameter elsewhere in the crystal. Formally, ξ is the correlation length of individual microscopic steps and it plays a crucial role in determining the overall kinetic behaviour.

Salje (1988*a*) finally rescaled equation 2 by introducing a second important length parameter, ξ_C, which represents the local length scale over which conservation occurs. (This concept is explained in detail in the following section). The final rate equation is:

$$\frac{dQ}{dt} = \frac{-\gamma \langle a^2 \rangle}{2RT} \left[1 - \frac{\xi_C^2}{\xi^2} \exp\left(\frac{\xi^2}{2} \nabla^2\right) \right] \frac{\partial G}{\partial Q} \quad (4)$$

Three solutions can be readily envisaged. Firstly, if the correlation length of Q is the same as the length scale over which conservation occurs, i.e. $\xi = \xi_C$, equation 4 becomes (after expanding the exponential and considering only the lowest order term—for small values of the exponent):

$$\frac{dQ}{dt} = \frac{\gamma \langle a^2 \rangle}{4RT} \xi_C^2 \nabla^2 \frac{\partial G}{\partial Q} \quad (5)$$

This is referred to as the Cahn (or C) equation (Metiu *et al.*, 1976*a,b*; Salje, 1988*a*) since it corresponds to the description of spinodal decomposition developed by Cahn (1961, 1962, 1968) and Hilliard (1970), (see also Langer, 1971). For spinodal decomposition, Q can be regarded as the amplitude of the composition modulation.

Secondly, in the limit that the correlation length of Q is large relative to the conservation length, i.e. $\xi_C/\xi \rightarrow 0$, equation 4 becomes:

$$\frac{dQ}{dt} = \frac{-\gamma \langle a^2 \rangle}{2RT} \frac{\partial G}{\partial Q} \quad (6)$$

which is referred to as the Ginzburg–Landau* (or GL) equation (Metiu *et al.*, 1976*a,b*; Lifshitz and Pitaevski, 1981; Salje, 1988*a*). The third solution is for $1 < \xi_C/\xi < 0$ and represents the general case as expressed by equation 4 itself.

An essential implication of this overall rate law is that, except in the limiting case of $\xi_C/\xi \rightarrow 0$, modulated structures should invariably develop, although they need not necessarily have large amplitudes or well defined wavelengths. This striking conclusion arises simply from the fact that the general solution of an equation of the form:

$$\frac{dQ}{dt} \propto \nabla^2 Q \quad (7)$$

* Salje (1988*a*) has used the term Ginzburg–Landau to describe this kinetic equation to distinguish it from the Landau–Ginzburg equation which describes equilibrium behaviour.

is a modulation in Q with wave vector k and amplitude $A(k,t)$ after time t. The amplitude, $A(k,t)$, will evolve as:

$$A(k,t) = A_o(k,o) \exp[\alpha(k) \cdot t] \qquad (8)$$

where $A_o(k,o)$ is the initial amplitude and $\alpha(k)$ is an amplification factor. In place of the amplification factor, a time constant, $\tau(k)$, is commonly used, though the relation between them is simply $\tau(k) = [2\alpha(k)]^{-1}$.

For most natural materials the behaviour of Q falls between the two limiting cases and the general solution applies. Mathematical complexities prevent this from being of practical value at present, however, but the properties of real systems can be approached successfully from both ends as $\xi_C/\xi \to 1$ (C) or $\xi_C/\xi \to 0$ (GL).

Physical insights: the significance of different length scales. From equation 4 it is immediately clear that the correlation length of the order parameter Q can have a profound influence on the kinetics of order/disorder processes. (The correlation length Q also has a pronounced effect on equilibrium behaviour, of course). There are other length scales involved, however, which can also significantly alter the way in which a system will evolve. For example, transition mechanisms may depend on individual atomic exchanges between neighbouring crystallographic sites in a crystal, i.e. on a microscopic scale. These may be associated with the development of modulations over tens to hundreds of unit cells, i.e. on a mesoscopic scale, which in turn are associated with free energy reductions of the crystal as a whole, i.e. on a macroscopic scale. In addition, the experimental techniques used to follow these changes will have their own intrinsic length scales so that microscopic, mesoscopic and macroscopic contributions can be examined separately. Nuclear magnetic resonance spectroscopy will give insights into the microscopic behaviour whereas the spontaneous strain will indicate the net macroscopic effect, and so on.

The order parameter, Q, is used here as a macroscopic thermodynamic quantity. It can also be understood in structural terms as, for example, the amount of displacement of atoms from their equilibrium positions in a high symmetry phase when it distorts to a low symmetry form by a displacive transition. If the translational symmetry is preserved in this example and the crystal is homogeneous, every atom moves in the same directional sense. The displacement of an individual atom is as representative of Q as the distortion of the crystal as a whole. For displacive transitions in which translational symmetry is lost (doubling

or tripling of the unit cell, etc.), however, or for order/disorder transitions, a number of atoms must be examined before the order parameter can be defined in an analogous geometrical manner. Even if the crystal is homogeneous on a macroscopic scale, it must be inhomogeneous on some atomic scale; a given structural site must contain either an A atom or a B atom although the average occupancy for that site across the whole crystal is fully defined as some intermediate value. In this case a local atomic scale order parameter, such as the number of 'correct' neighbours round a given site need not correspond directly with the macroscopic order parameter.

The length scales over which different order parameters operate effectively determine what is meant by a 'homogeneous' or 'inhomogeneous' crystal. On an atomistic scale a short range order parameter, σ, may be defined in terms of numbers of 'correct' or 'incorrect' bonds present, with respect to some ordered structure (i.e. in terms of pair correlations). On a mesoscopic scale the local order parameter, Q_1, may be defined in terms of site occupanies, lattice distortions, etc. In contrast with σ, Q_1 has a thermodynamic meaning because it involves a large number of atoms ($\geq 10^5$). For order/disorder systems these microscopic and mesoscopic order parameters are related, to a first approximation, by $Q_1^2 = \langle \sigma \rangle$, where the brackets signify the mean value, as may be shown by a Bragg-Williams type of approach, e.g. see Christian (1975) or Becker (1978). The macroscopic order parameter, Q, is then given by the average value of Q_1 throughout the whole crystal ($Q = \langle Q_1 \rangle$). The value of σ may vary locally within a mesoscopic domain to which a value of Q_1 is assigned. Q_1 can in turn vary between mesoscopic domains within a crystal without losing its thermodynamic significance. From a macroscopic, thermodynamic point of view, the crystal may be regarded as being homogeneous if $Q_1 = Q$ in all the mesoscopic regions and inhomogeneous otherwise.

The correlation length, ξ, of Q may be understood physically in terms of the distance over which a change in the value of Q in one area of a crystal will produce correlated changes in other areas. Of course, ξ will vary according to the restoring forces which operate and, if the restoring force for a small perturbation in Q goes to zero, the influence of the perturbation can extend to the whole crystal. ξ in fact diverges when T approaches a critical temperature, T_C, as:

$$\xi = r_{CO}\left(\frac{T - T_C}{T_C}\right)^{-\nu} \quad (\nu > 0) \qquad (9)$$

where r_{CO} is the correlation length of Q at $T =$ OK. For a second order transition T_C is the equilibrium transition temperature and $\nu = \frac{1}{2}$.

The magnitude of ξ can be determined experimentally by making use of the Ginzburg criterion, which states that Landau theory fails if spontaneous local fluctuations in Q become so large that they exceed the mean value of Q for the crystal (e.g. see Ginzburg et al., 1987). The temperature interval near T_C over which this occurs (where Q is small) is known as the Ginzburg interval, ΔT_G, and can be estimated from:

$$\Delta T_G = A \left(\frac{k_B}{\Delta C l^3}\right)^2 \cdot \left(\frac{l}{r_{CO}}\right)^6 \qquad (10)$$

where ΔC is the jump in specific heat at T_C, l is the interatomic length scale (e.g. a unit cell dimension), A is a constant on the order of $10^{-2} - 10^{-3}$, k_B is the Boltzmann constant and $(k_B/\Delta C \cdot l^3)$ is of the order of ~ 1 (Ginzburg et al., 1987; Salje, 1988b). The important point is that, for the structural phase transitions in minerals which have so far been investigated, ΔT_G appears to be very small, i.e. less than a few Kelvins. r_{CO} is probably on a mesoscopic to macroscopic scale, therefore, and no serious limitations to the applicability of Landau theory are anticipated in this context.

Loosely speaking, r_{CO} measures the length scale of the interactions which actually drive a particular phase transition. In framework silicates an important mechanism for producing long-range interactions is via elastic strains (Carpenter, 1988). One area of a crystal is influenced by the configuration adopted in neighbouring areas through the bending of the semi-flexible network of T–O–T bonds, where T is Al or Si in tetrahedral co-ordination and O is oxygen. More generally, transitions which involve large spontaneous strains appear to conform to this behaviour (Cowley, 1976; Folk et al., 1976; Als-Nielsen and Birgeneau, 1977). Examples are provided by As_2O_5 (Salje et al., 1987; Redfern and Salje, 1988), $NaNO_3$ (Poon and Salje, 1988; Reeder et al., 1988) and $CaCO_3$ (Redfern et al., 1989). On the other hand, magnetic phase transitions and transitions in related pseudo-spin systems show short correlation lengths (small r_{CO}), large Ginzburg intervals, significant deviations from Landau theory and, consequently, different kinetic behaviour than would be predicted purely on the basis of the GL rate equation. They will still conform to the generalized rate law (equation 6), however, with solutions as discussed by Binder (1987) for first order transitions.

In the case of time-dependent Landau theory there is one final length scale which plays a critical role in controlling which rate law will apply for a given system, the length scale of conservation, ξ_C. This concept is most easily explained with concrete examples. Take, first of all, a spinodal exsolution process. An increase in one component at a given position in the spinodal modulation is compensated exactly by a decrease in that component in adjacent areas. The length scale over which this conservation occurs is the length scale of the modulations themselves, typically ~ 100–1000 Å in silicates (Buseck et al., 1980; Yund, 1983, 1984). On the other hand, in an order/disorder process the net balance of exchange is only between neighbouring crystallographic sites in the structure and this interatomic distance, therefore, represents the conservation length. For the limiting case of a purely displacive transition, a displacement of one atom from its position in the high symmetry structure need not be accompanied by any compensatory movement of atoms in an opposite sense and the conservation length is strictly zero.

During spinodal exsolution, the effective correlation length of Q is on the order of the wavelength of the modulation, so that the ratio ξ_C/ξ tends to 1. For order/disorder and displacive processes in silicate minerals we have argued that the correlation length of Q can be on a mesoscopic scale so that the ratio ξ_C/ξ tends to zero. The C equation should, therefore, provide a correct description of the kinetics of spinodal decomposition but the GL equation should be used to describe the kinetics of order/disorder transitions. Very little is known about cases where the ratio ξ_C/ξ is between zero and one, such as might occur if ordering is accompanied by a degree of mass transport. Solutions for such processes must be derived from the full rate equation (equation 4) and will be mathematically complex.

Alternative rate laws for order/disorder transitions

In the previous discussion of the significance of correlation lengths it was intimated that the GL equation should provide a valid description of the kinetics of order/disorder transitions in framework silicates. Attempts have been made to use the Cahn equation to describe order/disorder kinetics in metals, however, by extrapolating it to progressively smaller wavelengths in a largely empirical manner (Cook, 1969; Cook and Hilliard, 1969; Cook et al., 1969; de Fontaine and Cook, 1971). A fundamental problem with the latter approach is that the continuum model, i.e. effectively Fick's second law, is not strictly

appropriate for diffusion distances on an individual unit cell scale. The approach is nevertheless illuminating of some of the important physical parameters involved and it is briefly summarized in this section before dealing at length with GL solutions.

Cahn equation for short wavelengths

Langer (1971) showed that a general equation in the form of equation 5 can be reduced to the more familiar diffusion equation of Cahn by choosing a simple macroscopic free energy function and using a parabolic approximation for the variation of free energy with composition. The Cahn/Hilliard expression for spinodal decomposition (see Hilliard, 1970) results as one possible solution from equation 4 using $\xi_C = \xi$.

$$\frac{\partial c}{\partial t} = D \cdot \nabla^2 c + \frac{D \cdot 2\eta^2 Y \nabla^2 c}{g''} - \frac{2KD\nabla^4 c}{g''} \quad (11)$$

where c is the concentration of a given atomic species, D is an effective interdiffusion coefficient, η is the linear strain per unit volume, Y is a function of the elastic constants of the material, g'' is the second derivative of the local free energy with respect to c, and K is the gradient energy coefficient. The first term on the right hand side of equation 11 effectively represents Fick's second law. The second term arises from the strain energy due to variations in lattice parameters in a compositionally modulated crystal, and the final term arises from the energy contributions due to the presence of steep concentration gradients. Solutions are of the form of equation 8 with the amplification factor, $\alpha(k)$, given by:

$$\alpha(k) = -D|k|^2 \left(1 + \frac{2\eta^2 Y}{g''} + \frac{2K}{g''} \cdot |k|^2\right) \quad (12)$$

Now, since it is possible to describe ordered structures in terms of composition modulations with wavelengths which are some fraction of the unit cell size, equations 11 and 12 might be used as a basis for treating the kinetics of ordering or disordering. For exsolution processes, steep concentration gradients are energetically unfavourable ($K > 0$) and g'' is negative. In systems with $g'' > 0$ and $K < 0$, steep concentration gradients will be energetically favourable and ordering may occur. Because of the simplifications introduced into the modified diffusion equation, particularly in linearizing the gradient term and the local energy term (g'' is assumed to be constant), however, the rate law strictly applies only for wavelengths which are considerably larger than the atomic spacings and for small amplitudes. Cook et al. (1969) were nevertheless able to derive a discrete solution for short wavelengths in a cubic lattice which required a relatively minor modification of the original continuum expression to include the contributions of higher order terms in k; $|k|^2$ is replaced by $B^2(k)$ where:

$$B^2(k) = \sum_r m(r) \quad \{1 - \cos[\overline{k} \cdot \overline{x}(r)]\} \quad (13)$$

The term $m(r)$ takes into account different jump frequencies for atoms moving into different neighbouring sites and r is the nearest neighbour site reached by vector $\overline{x}(r)$. Further adjustments can be made to the elastic energy in order to account for atomic scale anisotropies in elastic energies, or to the gradient energy in order to include the effects of higher-order terms, but these are increasingly complex.

From an experimental point of view the intensity of a satellite reflection, $I(k,t)$, is proportional to the square of the amplitude of the composition modulation, $A(k,t)$, and it is expected that:

$$I(k,t) = I(k,o) \exp[2\alpha(k)t] \quad (14)$$

A plot of $\ln[I(k,t)/I(k,o)]$ against t for the decay of a modulated phase should, therefore, be linear and for a disordering reaction this would give $\ln(Q^2) \propto t$.

Paulson and Hilliard (1977) have shown that the modified rate equation gives adequate agreement between experiment and theory for the decay of synthetically modulated Cu–Au alloys at least down to wavelengths of ~10 Å. Although the overall approach can be questioned in that it is based on the assumption that Fick's law remains approximately adequate for diffusion distances on a unit cell or interatomic scale, rate laws of the form $\ln I(k,t) \propto t$ are indeed observed for some disordering processes. Some of the phenomenological parameters could, in principle, be investigated experimentally to establish whether they have any real physical meaning. However, the same exponential decay of $I(k,t)$ may also occur in the GL limit and the observation of a particular rate law cannot of itself be taken as proof that a particular mechanism is operating. The nature of the length parameters, ξ and ξ_C, for a given system of interest should be considered before distinguishing between kinetic behaviour governed by the GL or C equations.

It is also of interest to note the k dependence of $\alpha(k)$ predicted by the modified version of the Cahn equation, with $B^2(k)$ replacing $|k|^2$ and $g'' > 0$, $K < 0$. The amplification factor is expected to have a maximum at the Brillouin zone boundary, to have minima between the zone centre and zone boundary and to extrapolate to zero at the
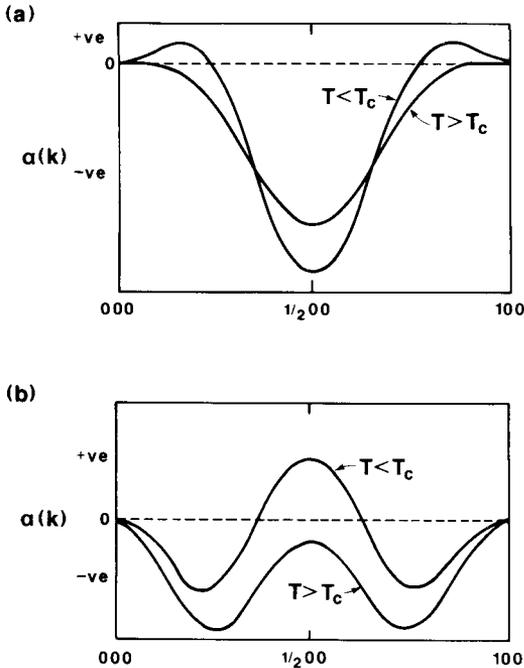
(a)

(b)

FIG. 1. Schematic variation of amplification factor, $\alpha(k)$, as a function of position in the Brillouin zone (shown along a^* for simplicity in this case). Positive $\alpha(k)$ implies that the modulation grows in amplitude and negative $\alpha(k)$ implies that it decays. (a) For spinodal decomposition: $g'' < 0$, $K > 0$. (b) For order/disorder: $g'' > 0$, $K < 0$. (N.B. the value of k at which $\alpha(k)$ is a maximum can vary with time during spinodal decomposition but remains constant during ordering or disordering.) After: Cook et al. (1969), Yamauchi and de Fontaine (1974).

zone centre (Fig. 1, after: Cook et al., 1969; Yamauchi and de Fontaine, 1974; Paulson and Hilliard, 1977).

For a recent review of the application of the Cahn equation see Hono and Hirano (1987).

Ginzburg–Landau solutions

Even though specific values for the two length parameters, ξ_C and ξ, are not usually known for order/disorder transitions in silicate minerals, there is sufficient evidence, as discussed above, to suggest that the ratio ξ_C/ξ is much closer to zero (GL) than to unity (C). If no chemical transport occurs, the GL equation (equation 6) is expected to provide a more valid description of cation order/disorder processes than the C equation, notwithstanding the adjustments which have been made to the latter for small wavelengths. Different specific rate laws can be obtained from the GL equation, however, depending on the precise nature of the physical processes which oper-

ate at the microscopic and macroscopic levels. The solutions can be as diverse as $Q^2 \propto \ln t$ and $\ln Q \propto t$.

An important and valuable aspect of the GL equation, in practical terms, is that the dependence of G on Q may be given explicitly using the conventional Landau free energy expansions derived for equilibrium conditions. Thus, for a second order transition in a material for which only a single, scalar order parameter is required:

$$G = \tfrac{1}{2}a(T - T_C)Q^2 + \tfrac{1}{4}bQ^4 \qquad (15)$$

This may be substituted directly into the GL equation to give:

$$\frac{dQ}{dt} = \frac{-\gamma\lambda\exp(-\Delta G^*/RT)}{2RT}$$

$$[a(T - T_C)Q + bQ^3] \qquad (16)$$

$$\Rightarrow t - t_o = \int_{Q_o}^{Q} \frac{-2RT}{\gamma\lambda\exp(-\Delta G^*/RT)}$$

$$\left(\frac{1}{a(T - T_C)Q + bQ^3}\right) dQ \qquad (17)$$

which may be solved easily for some isothermal annealing sequence at temperature T. The Landau coefficients and the value of T_C are identical, in this case, to those used to describe equilibrium behaviour as a function of T, and ΔG^* is the normal free energy of activation. The coefficients γ and λ have to be treated numerically as proportionality constants; they cannot easily be determined from first principle calculations.

Of course, tricritical, first-order or more complex formulations of the free energy may lead to differential equations which require either numerical solution or further simplifying assumptions. Nevertheless, the resulting rate laws have immediate practical applications in interpreting experimental data for wide ranges of t, T and Q. Before demonstrating these applications for specific minerals, it is necessary to summarize the most important situations envisaged by Salje (1988a).

Q remaining homogeneous. If crystals remain homogeneous in Q through an ordering or disordering experiment, i.e. Q increases or decreases continuously and homogeneously, solutions of the form given in equation 16 apply. These complete solutions are valid for long time intervals and large variations in Q; they also apply to ordering or disordering below T_C and to disordering above T_C (Fig. 2). The implication is that the sequence of structural states through which the crystals pass as a function of time at constant temperature is
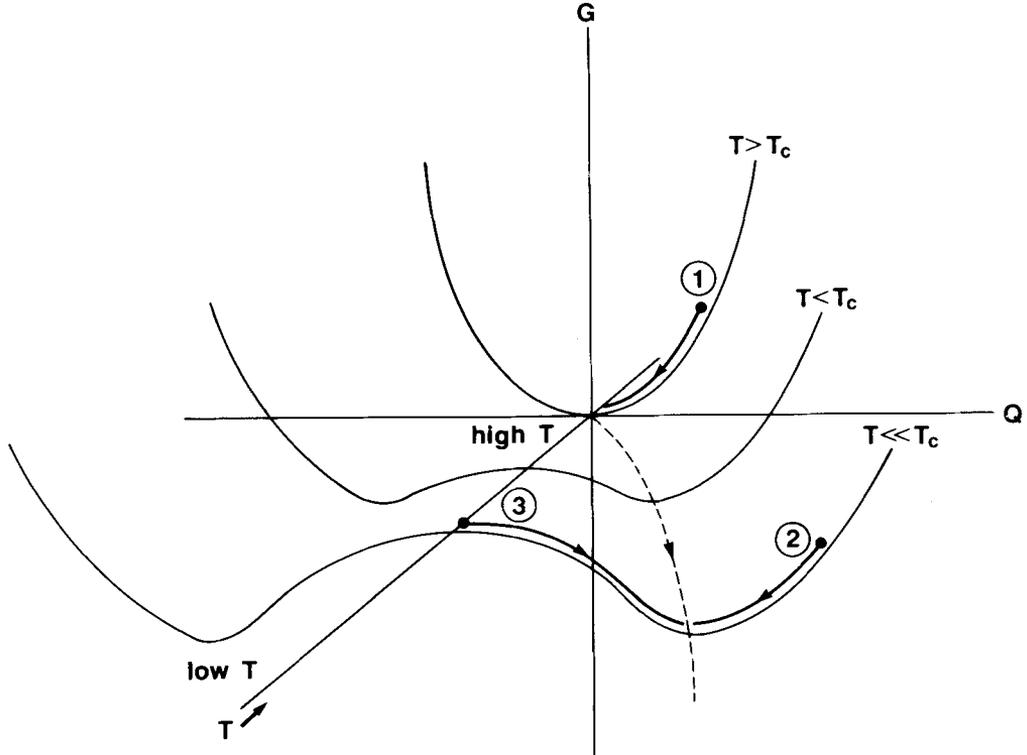
FIG. 2. Free energy (G)–order parameter (Q)–temperature (T) surface for a second-order transition showing the variation of Q during equilibrium cooling (dashed line), and during isothermal kinetic experiments for crystals which remain homogeneous in Q (heavy lines). Pathway 1: disordering above T_c; pathway 2: disordering below T_c; pathway 3: ordering below T_c.

identical with the sequence which would develop as a function of changing temperature under equilibrium conditions (Salje, 1988a).

Simpler solutions may be derived for small displacements, δQ, from the equilibrium value of Q, Q_{eq}, at a given annealing temperature. For the second-order case (equation 15), Salje (1988a) expanded $\partial G/\partial \delta Q$ about Q_{eq} and truncated the expansion after $(\delta Q)^2$ to give:

$$t - t_o = \frac{-RT}{\gamma\lambda\exp(-\Delta G^*/RT)bQ_{eq}^2}$$

$$\left[\ln\frac{\Delta Q}{\Delta Q_o} - \ln\left(\frac{3bQ_{eq}\Delta Q + 2bQ_{eq}^2}{3bQ_{eq}\Delta Q_o + 2bQ_{eq}^2}\right)\right] \quad (18)$$

where $\Delta Q = Q - Q_{eq}$ and $\Delta Q_o = Q_o - Q_{eq}$. Truncating the expression after terms in δQ (i.e. using a harmonic approximation, $(\partial G/\partial \delta Q) \propto \delta Q$) gives a simpler form valid for only a limited change of Q:

$$t - t_o = \frac{-RT}{\gamma\lambda\exp(-\Delta G^*/RT)bQ_{eq}^2} \cdot \ln\left(\frac{\Delta Q}{\Delta Q_o}\right) \quad (19)$$

i.e.

$$\ln\Delta Q \propto t \quad (20)$$

At temperatures close to T_C, equation 15 reduces to:

$$G \approx \tfrac{1}{4}bQ^4 \quad (21)$$

which, when substituted into the GL equation gives:

$$t - t_o = \frac{RT_C}{\gamma\lambda\exp(-\Delta G^*/RT)\cdot b}\left(\frac{1}{Q^2} - \frac{1}{Q_o^2}\right) \quad (22)$$

i.e.

$$\frac{1}{Q^2} \propto t \quad (23)$$

Fluctuations in Q. Within a crystal at equilibrium there will necessarily be local dynamical fluctuations in Q. The amplitudes of these fluctuations, from the dissipation–fluctuation theorem in the high-temperature limit (Salje, 1988a), are given by:

$$\langle(\delta Q)^2\rangle = k_B T\chi \quad (24)$$

where $\langle(\delta Q)^2\rangle$ is the mean value of the amplitude squared, k_B is the Boltzman constant; χ is the order parameter susceptibility defined as:

$$\chi^{-1} = \frac{\partial^2 G}{\partial Q^2} \qquad (25)$$

where the susceptibility varies with temperature as:

$$\chi \propto (T - T_C)^{-\gamma} \qquad (26)$$

with $\gamma = 1$ in Landau theory of a second-order phase transition. At equilibrium there is a restoring force for any fluctuation from Q_{eq} since, by definition, the crystal is at a minimum in G. Once the crystal has been rapidly heated (or cooled) to the temperature at which a kinetic experiment is performed, this restoring force no longer exists and the fluctuations may become significantly amplified. Their presence will obviously influence the excess free energy and the effect can be accounted for by including a gradient term in the Landau expression:

$$\Delta G = \int[\tfrac{1}{2}a(T - T_C)Q^2 +$$
$$\tfrac{1}{4}bQ^4 + \tfrac{1}{2}g(\Delta Q)^2]dV \qquad (27)$$

where the integration over volume V is necessary to make ΔG independent of composition. This is the simplest form of a Landau–Ginzburg potential in which the gradient energy coefficient g (a positive quantity) describes the contribution to the free energy of gradients in Q on a mesoscopic scale. (This term should not be confused with gradient term, K, from spinodal theory; the nomenclature is usually that g refers to gradients in Q whereas K refers to gradients in composition).

Salje (1988a) substituted equation 27 directly into the GL equation and obtained, for small deviations from Q_{eq}:

$$\frac{dQ}{dt} = -\frac{\Delta Q}{\tau} -$$

$$\frac{\gamma\lambda\exp(-\Delta G^*/RT)g\Delta^2 Q}{2RT} \qquad (28)$$

where τ is a time constant:

$$\tau = \frac{RT}{\gamma\lambda\exp(-\Delta G^*/RT)bQ_{eq}^2} \qquad (29)$$

This is the same as equation 19 but with the additional term in $g\nabla^2 Q$ to account for the presence of the fluctuations.

The behaviour of Q and its spatial variations in the crystal can be treated as the sum of Fourier components:

$$Q = \sum_k Q_k^{ikr} \qquad (30)$$

where Q_k is the amplitude of a Fourier component with wave vector k, and r is distance in the crystal. If it is assumed that the Fourier components are totally uncorrelated, the amplitude of each component follows equation 19, but with a different time constant, depending on its wave vector:

$$\ln \Delta Q \propto \frac{t - t_0}{\tau_k} \qquad (31)$$

where

$$\tau_k^{-1} = \tau^{-1} + \frac{\gamma\lambda(-\Delta G^*/RT)gk^2}{RT} \qquad (32)$$

This k-dependence of the time constant, τ_k, is illustrated in Fig. 3. The rate of change of Q will be fastest (smallest time constant) for waves with large k, i.e. at the Brillouin zone boundary. Changes in Q will occur most slowly for waves with small k, i.e. at, or near, the zone centre. It should be noted that this k-dependence is significantly different from that predicted by the modified C equation (compare Figs 1 and 3). (In order to produce a smooth variation in τ_k^{-1} at the zone boundary, it would actually be necessary to include a fourth order gradient term in equation 27).
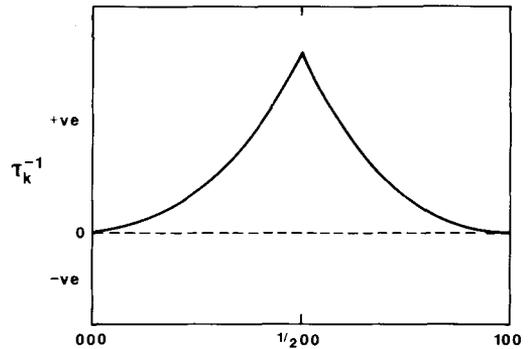

FIG. 3. Schematic variation of the k-dependent part of the time constant (i.e. $\tau_k^{-1} - \tau^{-1}$) as a function of wavelength (shown as position in the Brillouin zone along a^*) from a GL solution with fluctuation terms. The rate of amplification is a maximum (τ_k = minimum, τ_k^{-1} = maximum) at the Brillouin zone boundary and has the same sign for all waves. Note that in order to achieve a smooth variation at $\tfrac{1}{2}00$, higher order terms than are given in equation 32 would be needed.

There will also be an effect on the spread of k-vectors of Q which develops that is analogous to the development of fluctuations in a system at equilibrium. Fluctuations with long wavelengths do not consume much gradient energy [i.e. $\frac{1}{2}g(\nabla Q)^2$] and are consequently more common than those with short wavelengths. They also decay more slowly. A crystal in equilibrium at high temperatures contains more fluctuation waves at $k = 0$ than at k corresponding to a zone boundary point. If this crystal is quenched into the stability field of a differently ordered phase, the build up of the new ordered state can take advantage of these fluctuations. If the critical point for the ordering happens to be at the zone centre, many fluctuations with the correct k will already be present, but, in addition, there will be many with k close to zero and a rather broad k distribution of Q will develop at intermediate stages in the kinetic experiment. Zone boundary transitions, on the other hand, 'see' fewer fluctuations with approximately the correct k-vector and a sharper k dependence of Q can be expected. Since the different components have different time constants, a spread in the magnitudes of the
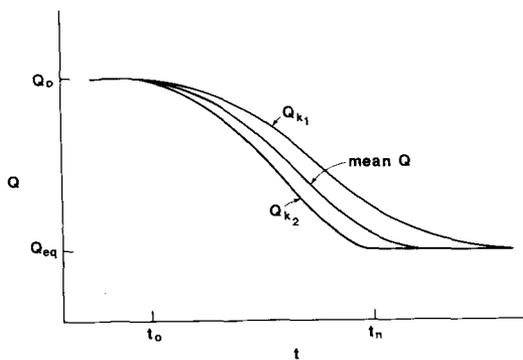
order parameter on a mesoscopic scale may develop with time, as illustrated for a disordering sequence in Fig. 4.

The circumstances in which fluctuations are likely to have the least impact on experimental observations occur for disordering of a crystal which is ordered on the basis of a zone boundary wave vector (superlattice reflection at Brillouin zone boundary). Such a crystal starts with a spectrum of Fourier components with a spread of amplitudes which has a sharp maximum at the zone boundary position in k-space. The Fourier component which decays fastest is that which predominates in the crystal, therefore, and other components have little chance of developing significant amplitudes. In other words, most of the disordering is achieved through the decay of a single Fourier component uniformly throughout the crystal, which remains homogeneous. Disordering of a crystal which is ordered on the basis of a zone centre wave vector, on the other hand, is more likely to involve the development of inhomogeneous variations in Q because of the slow decay of fluctuations with small k-vectors and the broader spread of the k-vector spectrum.

Ordering in a crystal which was perfectly homogeneous in Q on a mesoscopic scale, whether on the basis of a zone centre or zone boundary wave vector, would follow a GL rate law of the form given in equation 17. If any fluctuations were present, however, these would lead to increasing variations in Q because each component of the fluctuations would be amplified at a different rate. This, of course, corresponds to the normal picture of an ordering transition in which a range of Fourier components is amplified; nucleation may occur if different components become highly correlated such that individual ordered regions exceed the critical radius, e.g. in a first-order phase transition.

In all cases where heterogeneities develop, the spread of values of Q locally within the crystal initially increases. As equilibrium is approached, the amplitudes of fluctuations again become constrained by the free energy minimum with respect to Q, and the total spread of values about a mean value will diminish. Should any local region achieve $Q = Q_{eq}$ during the course of the experiment, e.g. at t_n in Fig. 4, these regions might act as nuclei which would grow at the expense of the remaining areas of crystal. Such nucleation can occur even when the transition would be thermodynamically continuous under equilibrium conditions. Salje (1988a) also showed that the heterogeneous spatial variations of Q which develop in this way might be sufficiently correlated to give a well-defined modulated structure. For

FIG. 4. Schematic variation of Q with annealing time, t, for a disordering transition in a crystal which is homogeneous at the start ($Q = Q_o$) and at equilibrium ($Q = Q_{eq}$). Inhomogeneities in Q develop throughout the crystal during the disordering process in this example due to the variation in the time constant, τ_k, with k for different Fourier components of Q. Pathways for the mean values of Q and for two limiting Fourier components ($k_2 > k_1$) are shown. At any given time the crystal has a range of values of Q given by the envelope of Q_{k_1} and Q_{k_2}. At a time, t_n, some regions of crystal may reach their equilibrium state of order ahead of others. These regions can act as nuclei and may grow at the expense of neighbouring regions which have lagged behind. For an ordering reaction Q_{eq} is greater than Q_o but the general behaviour would otherwise be the same.

example, if there is simply a range of Fourier components present in a crystal which is undergoing disordering, the component with largest τ_k (slowest rate of decay) would persist for the longest time. As the faster components decay away, this 'slow' component would remain as a poorly defined modulation. In other words, the modulated phase arises purely as a result of the kinetic process itself. In addition, however, the symmetry constraints which apply to equilibrium conditions no longer operate for an inhomogeneous crystal which is out of equilibrium; order parameter coupling which would not be allowed under equilibrium conditions can develop. Even at the GL limit of long correlation lengths, therefore, metastable modulated structures with rather well-defined wavelengths and orientations may appear. This general issue of 'kinetic' modulated phases is discussed at greater length in a later section.

The effect of 'local fields'. So far it has been assumed that, in a crystal which develops fluctuations in Q during a kinetic experiment, the heterogeneities do not in themselves influence the rate of ordering or disordering of individual mesoscopic regions. If, however, the local environment exerts a significant influence on the kinetics in a given region, and that local environment, or 'local field', is not the same as the average environment, or 'mean field', of the crystal as a whole, then a quite different result is obtained. Salje (1988a) illustrated the effect by using the analogy of a spin system in the mean field approximation.

Defining the order parameter σ for some local area of crystal, a possible mean field model yields:

$$\ln \sigma \propto t \left[1 - \tanh\left(\frac{M_{\text{eff}}}{RT}\right) \right] \qquad (33)$$

In this case M_{eff} is the effective field which is conjugated to σ and is seen by all regions of the crystal. The effective time constant is given by:

$$\tau^{-1} \propto \left[1 - \tanh\left(\frac{M_{\text{eff}}}{RT}\right) \right] \qquad (34)$$

If σ varies locally then M_{eff} will also vary locally and the probability of having a given local field will obviously depend on the probability of finding the appropriate configuration of local regions with particular values of σ. The mean value of σ for the crystal, $\langle\sigma\rangle$, then varies with time during a kinetic experiment according to the integral of all the local σ pathways, as controlled by their local fields. This integration yields, for a sufficiently broad Gaussian distribution of local confi-

gurations, a rate law of the form (over a limited time interval):

$$\langle\sigma\rangle \approx ART\ln t + B \qquad (35)$$

A and B are constants at constant temperature.

A similar analysis is achieved with the GL equation by describing the contributions of local fields in terms of local susceptibilities. In the harmonic approximation:

$$\frac{dG}{dQ} = \chi_{\text{eff}}^{-1} Q \qquad (36)$$

where χ_{eff}^{-1} is the effective susceptibility and consists of two parts:

$$\chi_{\text{eff}}^{-1} = \chi_{\text{h}}^{-1} + \chi_{\text{r}}^{-1} \qquad (37)$$

χ_{h}^{-1} is the normal susceptibility, as defined for a homogeneous crystal and χ_{r}^{-1} is the contribution of random fields arising from local inhomogeneities in Q or from any other effects, such as the presence of defects or impurities. Note that χ_{r}^{-1} operates on a mesoscopic or larger scale since it is defined in terms of Q, which is itself a mesoscopic or macroscopic parameter.

Individual regions which are homogeneous in Q follow the rate law given in equation 19 as:

$$\ln\frac{\Delta Q}{\Delta Q_{\text{o}}} \approx -\left(\frac{t - t_{\text{o}}}{\tau_{\text{eff}}}\right) \qquad (38)$$

though in this case the effective time constant, τ_{eff}, is given by:

$$\tau_{\text{eff}} = \frac{2RT}{\gamma\lambda\exp(-\Delta G^*/RT)} \cdot \frac{1}{(\chi_{\text{h}}^{-1} + \chi_{\text{r}}^{-1})} \qquad (39)$$

The variation with time of the mean value of ΔQ for the whole crystal ($\langle\Delta Q\rangle$) than depends on the probability distribution of χ_{eff}^{-1}, $P(\chi_{\text{eff}}^{-1})$. The mathematical procedure for integrating over all χ_{eff}^{-1} involves a Laplace transformation (Salje, 1988a; Salje and Wruck, 1988). For example, if $P(\chi_{\text{eff}}^{-1})$ is a delta function (Fig. 5a), i.e. χ_{eff}^{-1} is the same throughout the crystal, Q will remain homogeneous and the solution has the form of equations 19 and 20 ($\ln\Delta Q \propto t$). At the other extreme, if $P(\chi_{\text{eff}}^{-1})$ is a constant, P_{o}, all values of χ_{eff}^{-1} are equally probable (Fig. 5b) and the solution for long times and small deviations from equilibrium has the form:

$$\ln[\langle\Delta Q\rangle \cdot \Delta t] \propto \Delta t \cdot \chi_{\text{o}}^{-1} \qquad (40)$$

χ_{o}^{-1} is the effective susceptibility of the mean value of ΔQ after the integration over all χ_{eff}^{-1} and $\Delta t = t - t_{\text{o}}$, $\Delta Q = Q - Q_{\text{eq}}$. As usual, χ^{-1} will vary with T and may have a singularity as $T \Rightarrow T_{\text{C}}$.

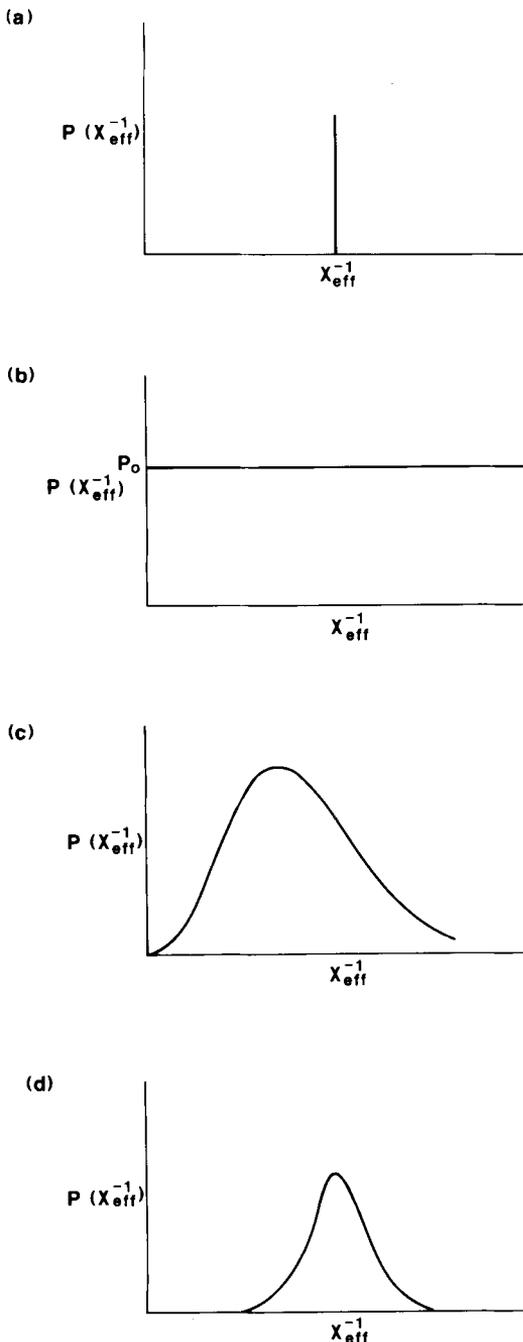Other $P(\chi_{\text{eff}}^{-1})$ distributions are also possible and

(a)

(b)

(c)

(d)

Fig. 5. Different probability distributions, $P(\chi_{\mathrm{eff}}^{-1})$, for the effective local susceptibility, χ_{eff}^{-1}, (schematic). (a) A delta function; χ_{eff}^{-1} is the same everywhere in the crystal. (b) Every value of χ_{eff}^{-1} has an equal probability, P_{o}, of occurring somewhere in the crystal. (c) Maxwell distribution. (d) Gaussian distribution.

each leads to a slightly different rate law. A Maxwell distribution (Fig. 5c) gives a rate law of the form:

$$\ln \langle \Delta Q \rangle \propto \sqrt{t} \qquad (41)$$

and Salje and Wruck also discuss the case of a Gaussian distribution (Fig. 5d) which gives a complex rate law involving the error function.

These rate laws derived from the GL equation are all based on a harmonic approximation for G as a function of ΔQ and strictly apply only for small deviations of Q from Q_{eq}. The important general features, however, are firstly that the rate law which operates in a given system may depend rather sensitively on the nature of inhomogeneities and defects present in the material. Secondly, the presence of such inhomogeneities in the starting crystals is likely to give rise to inhomogeneities in Q during the course of the kinetic experiment even if the final equilibrium state is homogeneous. Numerical solutions for wider ranges of Q and t can be obtained for individual cases if the free energy contribution of the local inhomogeneities or defects can be expressed formally in the $\partial G / \partial Q$ term of the GL equation.

In contrast with the behaviour of homogeneous crystals, the intermediate structural states which develop during annealing do not correspond with any equilibrium structural states. Each small region of crystal follows a path across its own free energy surface. This may be quite different from the free energy surface defined by Landau expansions of the usual form for predicting equilibrium, although some fluctuations might be close to dynamical fluctuations predicted by Landau–Ginzburg theory (i.e. including the gradient energy in equation 27). Because of interactions between adjacent regions, the free energy surfaces will also change with time and, unless discrete nuclei form, the individual regions will have continuous variations in Q and no well defined boundaries. Salje (1988a) refers to this as 'multivalley' behaviour.

An activation energy can always be introduced by scaling the time, t, with the time required for some elementary step, t'. The temperature dependence is:

$$t' \propto \exp\left(\frac{\Delta G^*}{RT}\right) \qquad (42)$$

Taking the simple mean field solution (equation 35):

$$\langle \sigma \rangle \propto RT \ln\left(\frac{t}{t'}\right) \qquad (43)$$

and hence:

$$\langle \sigma \rangle \propto RT\ln t - \frac{\Delta G^*}{RT} \qquad (44)$$

If we equate $\langle \sigma \rangle$ with Q^2 this gives:

$$Q^2 \propto RT\ln t - \frac{\Delta G^*}{RT} \qquad (45)$$

Coupling of ΔG^* with Q. Further variations in the rate laws for order/disorder processes may occur if the free energy of activation, ΔG^*, itself varies with Q. This can be understood physically if, for example, the energy barrier associated with breaking an aluminium–oxygen bond depends on whether the oxygen is also bonded to a silicon atom or an aluminium atom. The former would predominate in a crystal with an ordered distribution of Al, Si while the latter might exist in a disordered crystal. Other neighbouring atoms might also have an influence but, for strong, partly covalent bonds, it is unlikely that the overall effect could be large. In this case the enthalpy of activation, ΔH^*, is expected to remain effectively constant during an isothermal experiment. On the other hand, only a certain proportion of possible activated states will lead to a change of order in the desired direction, and this proportion may be sensitive to the state of order already attained. Thus, in a fully ordered state, almost any exchange of atoms will lead to a decrease in order, but when the crystal is already substantially disordered, only a small fraction of the total number of possible exchanges will lead to a further increase in disorder. The entropy of activation, ΔS^*, could depend sensitively on Q, with the result that ΔG^* will vary systematically during an isothermal kinetic experiment.

The coupling between Q and ΔG^* may be expressed formally as:

$$\Delta G^* = \Delta G_0^* + \varepsilon_G Q^2 \qquad (46)$$

and, since:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (47)$$

the coefficient, ε_G, can be split into enthalpy and entropy contributions:

$$\Delta G^* = \Delta H_0^* + \varepsilon_H Q^2 - T(\Delta S_0^* + \varepsilon_S Q^2) \qquad (48)$$

The GL equation then becomes:

$$\frac{dQ}{dt} = -\frac{\gamma\lambda\exp(-\Delta G_0^*/RT) \cdot \exp(-\varepsilon_G Q^2/RT)}{2RT}$$

$$\cdot \frac{\partial G}{\partial Q} \qquad (49)$$

If Q remains homogeneous, a simple solution for small deviations from equilibrium and for a limited time interval is obtained by using the harmonic approximation (i.e. using $\partial G/\partial Q = \chi^{-1}Q$). Salje (1988a) showed that this gives:

$$\ln\left(\frac{\Delta Q}{\Delta Q_o}\right) + \tfrac{1}{2}\Sigma\left[\left(\frac{\varepsilon_G}{RT}\right)^n \cdot \frac{Q^{2n}}{n \cdot n!}\right]_{Q_o}^{Q}$$

$$= \frac{-2RT\chi}{\gamma\lambda\exp(-\Delta G_0^*/RT)}(t - t_o) \quad (50)$$

If the coupling energy is small relative to the thermal energy ($\varepsilon_G \ll RT$) the series can be truncated to give:

$$\ln\frac{\Delta Q}{\Delta Q_o} + \frac{\varepsilon_G}{RT}(Q^2 - Q_o^2) =$$

$$\frac{-2RT\chi}{\gamma\lambda\exp(-\Delta G_0^*/RT)}(t - t_o) \quad (51)$$

Numerical solutions of equation 49 may be required if the simplifying assumptions needed to reach equation 51 are considered undesirable. Since ΔG^* is just a phenomenological parameter, its physical origin may not always be obvious. In most cases of order/disorder transitions in minerals, however, it is likely to correspond to microscopic activated states involving exchange of ions between neighbouring crystallographic sites.

Origin of modulated phases during kinetic experiments

One mechanism for producing incommensurate structures under equilibrium conditions is by the direct coupling of one order parameter, Q_1, with gradient terms of a second order parameter, Q_2 (Landau and Lifshitz, 1980). The simplest Landau expansion to describe this behaviour for equilibrium conditions has the form:

$$G = \tfrac{1}{2}a(T - T_C)(Q_1^2 + Q_2^2) + \tfrac{1}{4}b(Q_1^4 + Q_2^4) +$$

$$\ldots + d[Q_1(\nabla Q_2) - Q_2(\nabla Q_1)]$$

$$+ e[(\nabla Q_1)^2 + (\nabla Q_2)^2] \quad (52)$$

A solution of this expansion at $(dG/dQ) = 0$ has Q_1 and Q_2 as sinusoidal functions of distance in the crystal. Alternatively, the coupling might occur indirectly via the spontaneous strain (Salje and Devarajan, 1986). In either case, the appropriate Landau free energy function may be substituted into the GL equation to predict time-dependent behaviour. By implication, an incommensurate phase could occur during a kinetic experiment if the kinetic pathway is across the

same free energy-order parameter surface as defined by the equilibrium expansion. This incommensurate phase need not be the equilibrium state at the particular annealing pressure and temperature.

Under non-equilibrium conditions there are additional possibilities for producing modulated structures, either because of the effects of inhomogeneities in Q or because the relaxation of symmetry constraints allows other forms of coupling. A simple variation in the time constants of independent Fourier components of a single order parameter in an inhomogeneous crystal, as discussed above, will tend to leave only a poorly defined k-vector, however. More clearly defined modulations are likely to develop when coupling effects give preferred wavelengths and orientations.

Given that framework silicates often appear to require more than one order parameter to describe their structural states, it is to be expected that modulated structures will frequently develop during kinetic experiments. A particularly important class of coupling mechanisms involves separate displacive, Q, and order/disorder, Q_{OD}, contributions, as in cordierite (Salje, 1987a; Putnis et al., 1987) and feldspars (Salje, 1985, 1987b; Salje et al., 1985; Redfern and Salje, 1987; Carpenter, 1988). Also, since many phase transitions in nature occur under non-equilibrium conditions, these 'kinetic' modulated phases must play a role in determining the structural and thermodynamic evolution of some important rock-forming minerals. This brief discussion only touches on the more general issue of the stability of incommensurate superstructures, however. For a fuller description of the origin of incommensurate structures in minerals, readers are referred to the work of McConnell and Heine (Heine and McConnell, 1984; McConnell and Heine, 1985; McConnell, 1988; and references therein).

Experimental analysis

Experimental verification of these rate laws is, in principle, relatively straightforward. Two parameters must be measured as a function of time and temperature, the mean value of Q and the spread of Q within each sample. The order parameter is not measured directly but, as in studies of equilibrium behaviour, indirectly through any physical property which varies in a definable way with Q. Measurements can be made of lattice parameters, to give the variation of Q through the spontaneous strain, intensities and broadening of superlattice reflections, birefringence, frequencies and line widths of selected modes in vibrational spectra, nuclear magnetic resonance spectral peak intensities, etc. Given the variability of possible rate laws for ordering and disordering processes, it is often advisable to plot data on TTT diagrams initially. This does not involve the assumption of any particular rate law and will highlight changes in mechanisms or systematic variations in ΔH^* as a function of temperature or reaction progress (Putnis and McConnell, 1980).

Appropriate kinetic data which may be used to follow the evolution of the order parameter in a cation ordering or disordering reaction exist only for a limited number of mineral systems. These are used to illustrate practical implications of the overall approach reviewed above.

Zone boundary disordering (omphacite). Ordering of Mg/Al and Na/Ca on $M1$ and $M11$ and $M2$ and $M21$ sites in the pyroxene structure leads to a symmetry reduction from $C2/c$ to $P2/n$ in natural omphacite with compositions close to

$$\sim Na_{0.5}Ca_{0.5}Mg_{0.5}Al_{0.5}Si_2O_6$$

(see recent reviews by: Cameron and Papike, 1981; Carpenter, 1983; Rossi et al., 1983). Disordering above T_C can be followed by observing changes in the intensities, I_k, of superlattice reflections in crystals which have been annealed and then quenched. These reflections appear to decrease continuously with annealing time at a given temperature, while remaining sharp (Fleet et al., 1978; Carpenter, 1981; Carpenter et al., 1989b). Since I_k is proportional to Q^2, the disordering process, therefore, seems to involve a homogeneous and continuous decrease in the amplitude, Q_k, of a single Fourier component of Q. The transition is associated with a point on the Brillouin zone boundary and this Fourier component is expected to have the smallest time constant (fastest rate of decay).

The disordering behaviour observed by Carpenter et al. (1989b) follows $Q^2 \propto \sim \ln t$ for a considerable range of Q (Fig. 6) rather than $\ln \Delta Q \propto t$, as would be expected for the simplest, homogeneous GL behaviour. A satisfactory fit between the observations and a GL solution was obtained by using a tricritical model for the free energy driving force:

$$G = \tfrac{1}{2}a(T - T_C)Q^2 + \tfrac{1}{6}cQ^6 \qquad (53)$$

and a systematic dependence of ΔS^* on Q^2, as:

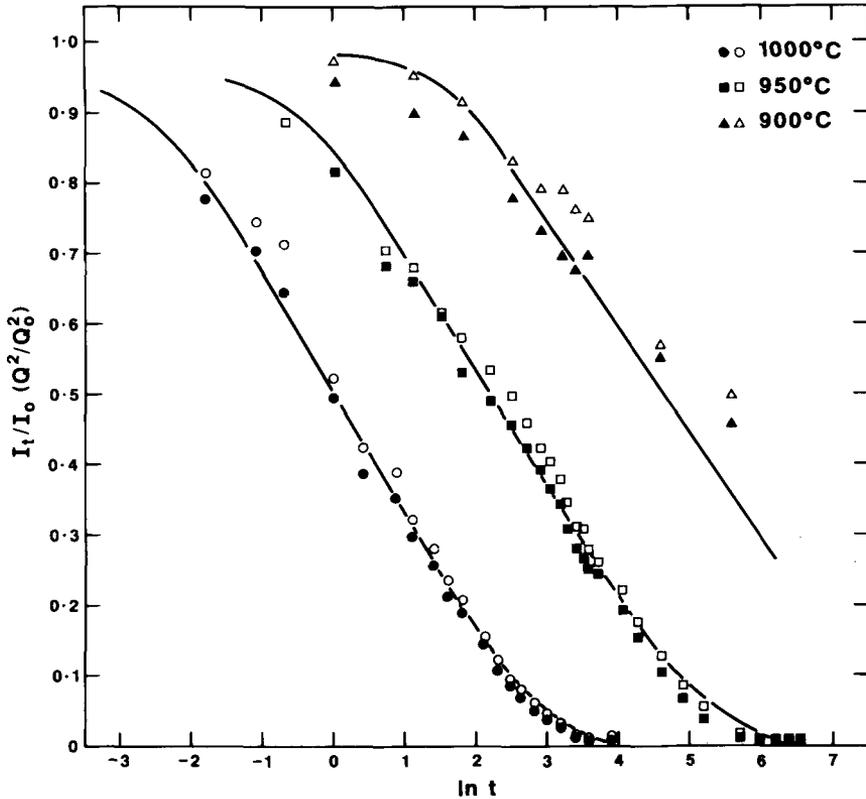$$\Delta S^* = \Delta S_0^* + \varepsilon_s Q^2 \qquad (54)$$

FIG. 6. Variation of the intensities of superlattice reflections $[I_t/I_o = (Q/Q_o)^2]$ with logarithm of annealing time for disordering in omphacite (from Carpenter *et al.*, 1989*b*). Solid lines: calculated from equation 55, with coupling between ΔS^* and Q^2. Open symbols from intensity measurements of 050 (relative to 060), filled symbols from measurements of $\overline{1}01$ (relative to $\overline{2}02$) reflexions, for crystals quenched from their annealing temperature of 1000, 950 or 900 °C.

This gives a GL equation of the form:

$$\int_{t_o}^{t} dt = \int_{Q_o}^{Q} \frac{-2RT}{\gamma\lambda\exp(-\Delta G_o^*/RT)} \cdot$$

$$\frac{\exp(-\varepsilon_s Q^2/R)}{[a(T - T_C)Q + cQ^5]} \cdot dQ \quad (55)$$

Values of $T_C = 865\,°C$, $a = 22.8\,J \cdot mole^{-1} \cdot K^{-1}$ and $c = 25\,900\,J \cdot mole^{-1}$ were derived from an analysis of experimental and structural data (Carpenter *et al.*, 1989*a*), and ΔH^* between ~540 and 580 kJ $\cdot$ mole^{-1} (at one atmosphere) from a TTT analysis of the kinetic data (Carpenter *et al.*, 1989*b*). Numerical solutions with $[\exp(-\Delta S_o^*/R)]/\gamma\lambda = 9 \times 10^{-19}$ secs and $\varepsilon_s = 20\,J \cdot mole^{-1}$ $\cdot K^{-1}$ are shown in Fig. 6.

Zone boundary ordering (anorthite). Al/Si ordering in anorthite ($CaAl_2Si_2O_8$) gives rise to a doubling of the triclinic feldspar unit cell (for

recent reviews see Ribbe, 1983*a*,*b*; Smith, 1983, 1984; Smith and Brown, 1988; Carpenter, 1988). The symmetry change is defined, for convenience, as $C\overline{1} \rightleftharpoons I\overline{1}$. T_C for this transition is well above the melting point but crystals with substantial Al/ Si disorder can be synthesized by annealing glass of anorthite composition for short times at temperatures above ~1100 °C (Laves and Goldsmith, 1955; Goldsmith and Laves, 1956; Kroll and Müller, 1980). Under these synthesis conditions, the first crystals to form give very diffuse intensity around $h + k = odd, l = odd$ superlattice positions in over-exposed electron diffraction patterns. On further isothermal annealing, diffuse but quite discrete reflections develop as pairs about these superlattice positions, closely resembling the so-called 'e' reflections of the incommensurate structure at intermediate compositions in the plagioclase feldspar solid solution ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$). On further annealing the incom-

mensurate reflections give way to progressively stronger and sharper reflections at the superlattice positions themselves.

The ordering transition under metastable conditions clearly proceeds by the amplification of a spectrum of Fourier components of Q with different wavevectors centred around superlattice positions in the reciprocal lattice. The incommensurate structure which develops at relatively small Q_{OD} may arise entirely as a consequence of the kinetic process or because it can exist as a stable equilibrium state over some temperature range between the stability fields of $C\bar{1}$ and $I\bar{1}$ structures. In either case, additional gradient or coupling terms must be included in the Landau–Ginzburg expansion to describe the free energy driving force for ordering. A possible source of coupling terms is the order parameter, Q, for a displacive monoclinic $(C2/m) \rightleftharpoons$ triclinic $(C\bar{1})$ transition in anorthite. T_C for this transition would be similar to or higher than T_C for the $C\bar{1} \rightleftharpoons I\bar{1}$ transition (Carpenter, 1988). Alternatively, coupling with a $C\bar{1}$ Al/Si ordering scheme might occur. This remains to be characterized, however, though an indirect coupling mechanism, via the spontaneous strain, is suspected. For present purposes it is sufficient to note that, as expected from theory, the metastable conditions of a kinetic experiment promote the development of a modulated structure.

Solution calorimetric data show that the excess enthalpy associated with the transition increases in magnitude (becomes more negative) approximately linearly with the logarithm of annealing time at constant temperature (Fig. 7, from Carpenter, 1988). Although numerical values for the macroscopic order parameter associated with the Al/Si ordering, Q_{OD}, have not been obtained for the synthetic samples, estimates of the Landau
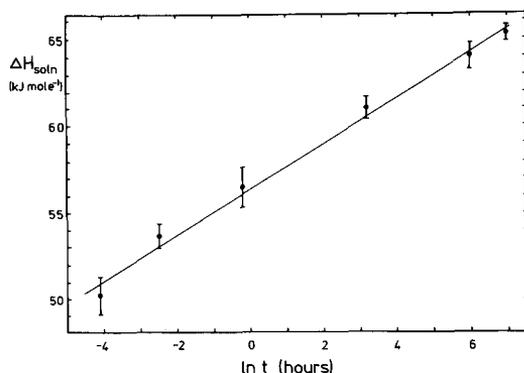
FIG. 7. Variation of enthalpy with logarithm of annealing time ($\Delta H \propto -\Delta H_{soln}$, from solution calorimetry), for Al/Si ordering in anorthite at 1200 °C (from Carpenter, 1988).

coefficients for equilibrium behavior suggest that the transition may be close to being tricritical in character (Carpenter, 1988). For Q_{OD} between 0 and ~0.6 the excess enthalpy would be approximately proportional to Q_{OD}^2. If the inhomogeneities in Q are ignored, preliminary experiments at different annealing temperatures (Carpenter, in preparation) give results which can be described for a limited range of Q_{OD} using a rate law of the form:

$$Q_{OD}^2 \propto A\ln t + \frac{\Delta H^*}{RT} \qquad (56)$$

with ΔH^* between 400 and 500 kJ $\cdot$ mole^{-1}. The A coefficient appears to be temperature dependent, however, and the linearity of Q^2 with ln$t$ is not as well defined as in the case of cordierite (see below).

It is also possible to describe the ordering kinetics from a microscopic point of view. As in the case of cordierite (below), a separate order parameter, σ, describes the state of Al/Si order on a microscopic scale. This parameter is expected to be related to Q_{OD} via:

$$\langle \sigma \rangle = Q_{OD}^2 \qquad (57)$$

and is proportional to the number of nearest neighbour tetrahedral cation site linkages of the form Al–O–Al. If the enthalpy change, Δh, for each exchange reaction of the form:

$$(-Al-O-Al-) +$$
$$(-Si-O-Si-) \rightarrow$$
$$2(-Al-O-Si-) \qquad (58)$$
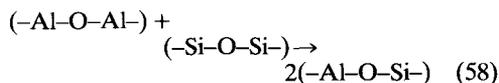
is constant, then the total enthalpy change could be understood in terms of a logarithmic decrease in the number of Al–O–Al bonds. Other contributions to the excess enthalpy, such as the elastic energy, will be small. The microscopic mechanism may include some dependence of the entropy of activation on σ to give a $\sigma \propto \ln t$ rate law. The mesoscopic mechanism clearly involves inhomogeneities in Q_{OD}, however, and the inhomogeneous behaviour can itself lead to a rate law of this form (e.g. equation 35).

Zone centre disordering (albite). The monoclinic $(C2/m) \rightleftharpoons$ triclinic $(C\bar{1})$ transition in albite $(NaAlSi_3O_8)$ involves two order parameters; Q_{OD} describes the contribution of Al/Si ordering and Q describes the contribution of atomic displacements in lowering the symmetry. Bilinear coupling occurs via the spontaneous strain and the evolution of both order parameters can be followed from measurements of lattice parameters (Salje, 1985; Salje *et al.*, 1985). Under equilibrium conditions, albite crystals are homo-
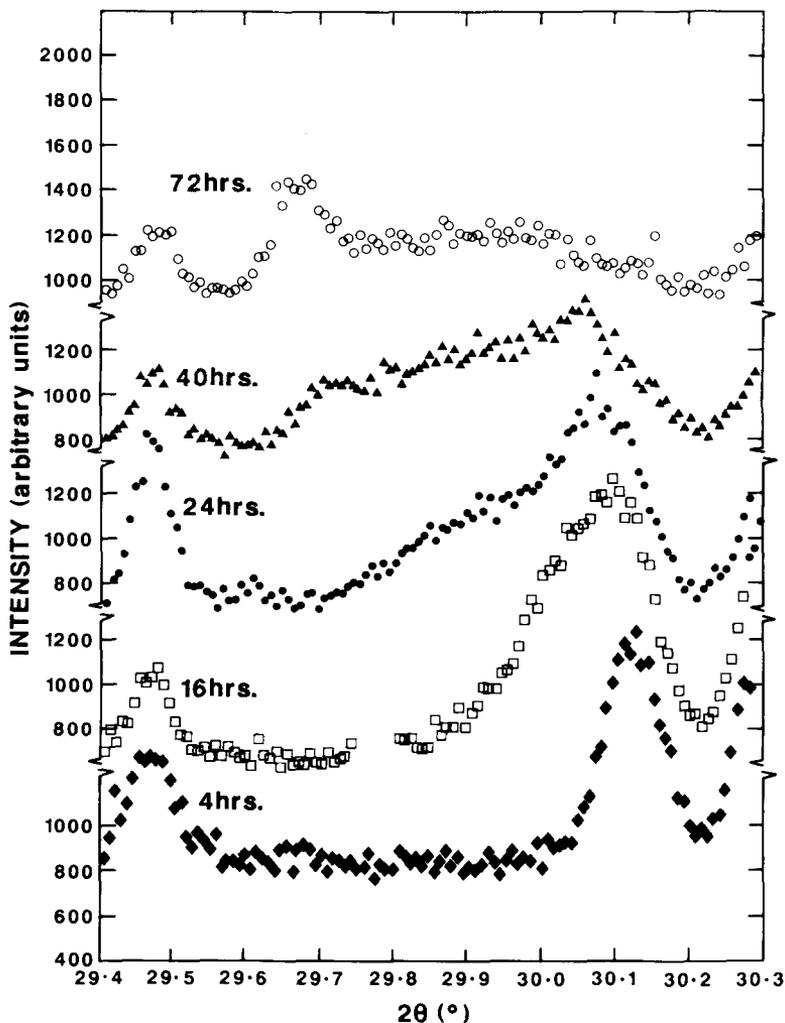
FIG. 8. Inhomogeneities in the degree of order of albite progressively disordered at 1080 °C, as revealed by line broadening in X-ray powder diffraction data (synchrotron source). At short annealing times, the 131 peak at $2\theta \approx 30.1$ °C is relatively sharp. After intermediate annealing times, the peak becomes increasingly broad until, after long annealing times, it begins to sharpen up at $2\theta \approx 29.7$ °C. The inhomogeneity is associated with the development of modulations in Q_{OD} during disordering.

geneous with respect to both Q and Q_{OD}, at least on a mesoscopic scale, and no modulated structures are known.

Salje and co-workers have recently found that modulations develop during isothermal disordering of ordered albite above T_C. These appear to be a consequence entirely of kinetic controls, with line broadening of X-ray diffraction maxima showing substantial local variations in Q and Q_{OD} (Fig. 8). The rate law for disordering at short times, using the spontaneous strain to follow Q_{OD}

on a macroscopic scale, appears to be of the form:

$$\ln Q_{OD} \propto t \tag{59}$$

The behaviour of substantially disordered material can be represented approximately as:

$$Q_{OD} \propto \ln t \tag{60}$$

If the kinetic behaviour is determined on a more local scale (e.g. using spectroscopic methods), similar rate laws are found for the average order

parameter. The time evolution of $\langle Q_{OD} \rangle$ measured on either length scale is identical, therefore.

Again as expected from theoretical considerations, zone centre disordering (albite) leads to significant inhomogeneities in Q and Q_{OD} whereas, during zone boundary disordering (omphacite), crystals remain homogeneous. This reflects the likelihood that the most important Fourier component has the fastest rate of decay in the zone boundary case but the slowest rate of decay in the zone centre case. Whether this is a truly general rule remains to be seen, however.

A modulated structure is commonly found in natural samples of potassium-rich alkali feldspar (reviewed by: Ribbe, 1983a,b; McLaren, 1984; Smith and Brown, 1988) and its origin as being a consequence of metastable ordering below T_C has been the subject of much speculation (see Smith and Brown, 1988; Carpenter and Putnis, 1985). Disordering of well-ordered triclinic crystals follows $Q_{OD}^2 \propto \ln t$ at one atmosphere (Carpenter, 1988). The kinetic data are extremely limited, but the macroscopic approach presented here clearly provides a basis for systematic studies of the evolution of both natural and experimentally heat treated samples.

Zone centre ordering (cordierite). Glass of cordierite composition ($Mg_2Al_4Si_5O_{18}$) crystallizes readily at temperatures of ~ 1000–$1450\,°C$ and the first-formed crystals are hexagonal with substantial Al/Si disorder between tetrahedral sites. On annealing at constant temperature the degree of Al/Si order increases and a modulated structure, consisting of two orthogonal transverse modulations, develops. On further annealing, the modulated structure gives way to a twinned orthorhombic structure (Putnis, 1980a,b; Putnis and Bish, 1983). As in the case of albite, two order parameters are required to define the thermodynamic behaviour. Q_{OD} refers to Al/Si ordering and Q to distortions from hexagonal symmetry (Salje, 1987a; Putnis et al., 1987). Q and Q_{OD} are actually two-dimensional because of the high symmetry involved, but this has little bearing on the simple kinetic analysis presented here.

A microscopic order parameter, σ, is given by:

$$\sigma = \left(1 - \frac{N}{3 \cdot 3}\right) \qquad (61)$$

where N is the number of Al–O–Al linkages per unit cell and is expected to be zero in the fully ordered orthorhombic structure.

Mean values of N and, hence, σ have been obtained for several isothermal series spanning the hexagonal, modulated and orthorhombic states by magic angle sample spinning NMR
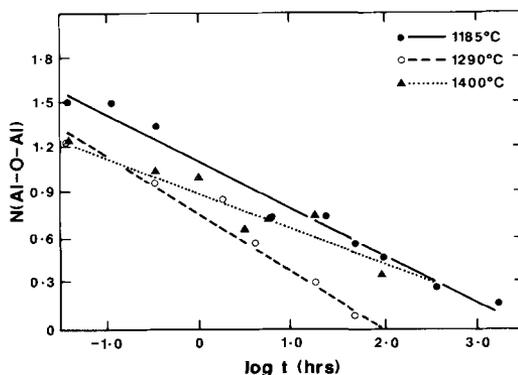

FIG. 9. Variation in number, N, of Al–O–Al linkages as a function of log (annealing time) for Al/Si ordering in cordierite at different temperatures (from Putnis et al., 1987). The 1185 and 1290 °C data have very different slopes from the 1400 °C data, perhaps suggesting the operation of a different ordering mechanism above and below $\sim 1300\,°C$.

spectroscopy (Putnis, 1988; Putnis et al., 1985, 1987; Putnis and Angel, 1985) and by infrared spectroscopy (Güttler et al., 1988). These are shown in Fig. 9 and imply a rate law of the form:

$$\sigma \propto ART \ln t + B \qquad (62)$$

It appears that the A coefficient varies with temperature, but this aspect of the behaviour is not yet fully understood. The TTT analysis of Putnis and Bish (1983) suggested that a change in the microscopic ordering mechanism occurs at $\sim 1300\,°C$, which would account for the substantial difference in slope between the NMR data above and below this temperature, however (see Fig. 9).

According to equation 44 the temperature dependence of B in equation 62 should give an estimate of the activation energy. Using the 1195 and 1290 °C data in Fig. 9, a value for ΔH^* of ~ 410–$590\,kJ \cdot mole^{-1}$ is obtained, which is consistent with the value of $500 \pm 40\,kJ \cdot mole^{-1}$ given by Putnis and Bish (1983).

Combined calorimetric data (Carpenter et al., 1983) and NMR data (Putnis and Angel, 1985) suggest that Δh for individual Al/Si exchanges does not vary with Q or Q_{OD} and Carpenter et al. (1983) expressed the microscopic rate law as:

$$\frac{dN}{dt} \propto e^{-N} \qquad (63)$$

This is equivalent to equation 61, since σ is proportional to N. The kinetic and thermodynamic data are insufficient to probe these rate laws further at this stage, but one possible interpre-

tation of the macroscopic behaviour is that ΔG^* varies with σ. The presence of modulations clearly shows that Q_{OD} and Q become inhomogeneous on a mesoscopic scale, however, and an alternative explanation involving the influence of local fields may be more realistic. That a modulated phase appears by coupling between order parameters under metastable conditions (Salje, 1987a; McConnell, 1985, 1988) is not at all surprising in the light of the other experimental observations and theoretical considerations discussed above.

Disordering of incommensurate phases. In general it is likely that order parameters for incommensurate phases have rather long correlation lengths. Apart from this, the kinetics of order/disorder processes should depend on the same factors as for commensurate transitions. Limited data exist for the time dependence of order parameter changes in such systems but disordering data for nepheline ($\sim Na_3KAl_4Si_4O_{16}$) are sufficient to illustrate the important issues, at least.

McConnell (1981) followed the intensities of incommensurate superlattice reflections from a natural nepheline *in situ* at temperatures up to 150 °C. On heating, the reflections show a sharp initial decrease in intensity, corresponding to rapid atomic displacements, followed by a slower decay associated with the disordering of potassium ions and vacancies between large cavity sites (McConnell, 1981, 1985). The reflections remain sharp during the disordering process suggesting that crystals remain homogeneous in Q. T_C is estimated as ~ 183 °C and the intensity data after relatively long annealing times at 100, 125 and 150 °C are consistent with second-order character for the transition (Fig. 10a).

Close to T_C, the GL solution for a homogeneous crystal approximates to $1/Q^2 \propto t$ (equation 22) and the intensity data obtained by McConnell at 150 °C are consistent with this, assuming $I_k \propto Q^2$ (Fig. 10b). At 100 °C and 125 °C the rate law appears to be closer to $\ln(Q-Q_{eq}) \propto t$ (Fig. 10c), which is the simplest solution for a homogeneous crystal. A TTT treatment of the data gives $\Delta H^* \approx 70 \, \text{kJ} \cdot \text{mole}^{-1}$, and suggests that ΔH^* does not obviously vary systematically with Q (Fig. 10d). McConnell (1981) obtained $81 \pm 12 \, \text{kJ} \cdot \text{mole}^{-1}$ by assuming a linear relation between I_k and t over a limited range of t at each temperature.

These intensity data are obviously not adequate to determine the rate laws unambiguously but they are at least consistent with simple GL solutions. A change from $\ln \Delta Q \propto t$ behaviour below T_C (nepheline) to $Q^2 \propto \ln t$ behaviour above T_C (omphacite) could be rationalized if ΔS^* varies with Q^2 at $T > T_C$ but not at $T < T_C$. Above T_C almost any activated state will lead to a decrease in order initially but the proportion will be reduced as Q diminishes. Below T_C, on the other hand, the change of order must be directed towards an equilibrium state which still has a high degree of order and each step is more likely to be constrained by the same proportion of appropriate activated states.

Conclusions

We have made no attempt to justify the mathematical basis of the rate laws presented in this paper. Interested readers are referred to the original papers of Glauber (1963), Langer (1971), Metiu *et al.* (1976a,b) and Salje (1988a) for the full derivations. Rather, we have intended to demonstrate that the use of time-dependent Landau theory provides a new and practical approach for quantifying the kinetics and mechanisms of order/disorder transitions.

It is anticipated that cation ordering processes in minerals will generally involve long correlation lengths and that the important ratio ξ_C/ξ tends to zero. As a result, the Ginzburg–Landau equation should provide a general kinetic solution. Specific rate laws then depend on the location of the critical point in the Brillouin zone, the presence of impurities and defects or inhomogeneities in Q, on whether ordering or disordering is being investigated, etc. These solutions should have much broader applications than many atomistic models since they are largely independent of the structural details of individual minerals. Use of the order parameter as the principle variable also has practical advantages in that, because of its relationship with other physical properties such as birefringence, spontaneous strain, diffraction characteristics, etc., its evolution can be followed with relatively simple experimental techniques. Furthermore, the thermodynamic driving forces can be expressed as Landau expansions in the same order parameter and these expansions seem to be effective for describing phase transitions in minerals over large temperature ranges of geological interest.

Given that so many different experimental techniques now exist for measuring order parameter behaviour on almost all length scales, it should be possible to determine the relative importance of microscopic processes, on the one hand, such as atomic interchanges, and macroscopic thermodynamic and physical properties, on the other, in controlling the non-equilibrium evolution of minerals. The common occurrence of modulated structures during kinetic experiments implies that mesoscopic scale processes are important. To
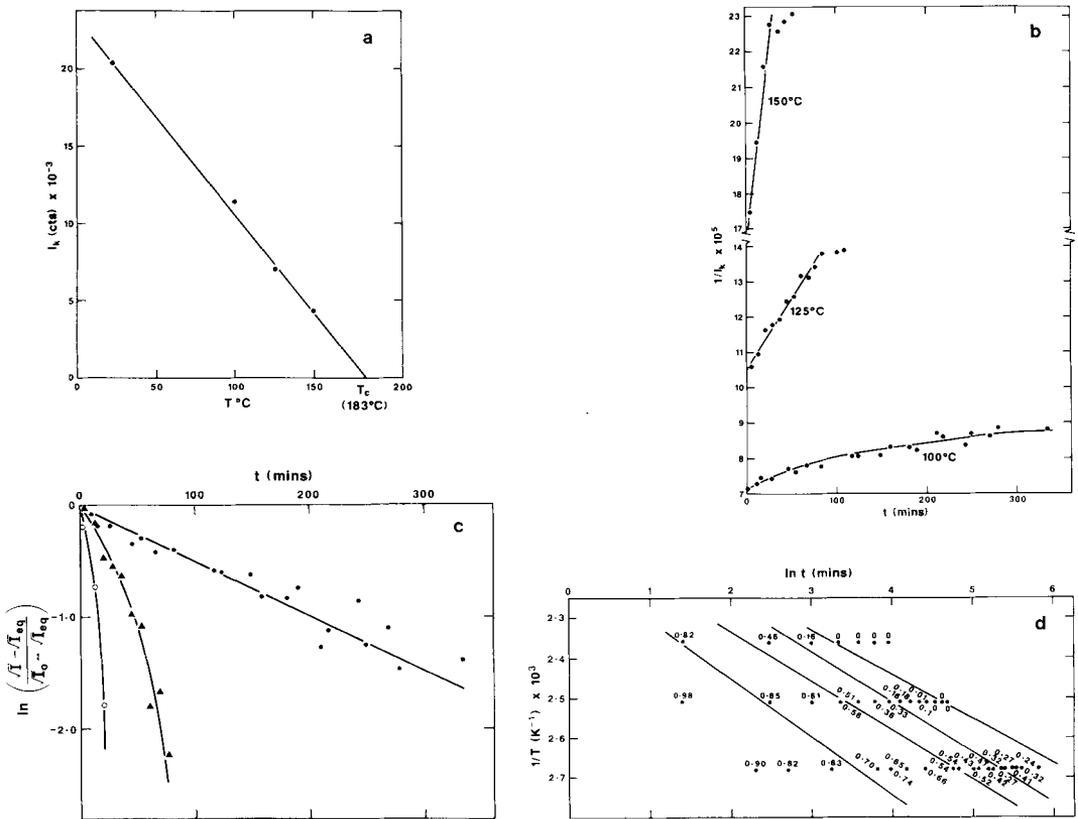
FIG. 10. Variations with time and temperature of the intensity, I_k, of an incommensurate superlattice reflection of nepheline. All data from McConnell (1981). (a) Intensity after long annealing times at 100, 125 and 150 °C and of the single-crystal starting material (25 °C). Although limited, the data are consistent with a second order transition at $T_C = 183$ °C (after McConnell, 1981). (b) Variation of $1/I_k$ ($\alpha 1/Q^2$) with time. The lines are drawn in between data points by eye. At 125 and 150 °C, the data are consistent with a rate law of the form $1/Q^2 \propto t$. (c) The same data as in (b) but replotted as $\ln[(\sqrt{I} - \sqrt{I_{eq}})/(\sqrt{I_o} - \sqrt{I_{eq}})]$, $[\propto \ln(Q - Q_{eq})/(Q_o - Q_{eq})]$, where I_{eq} is the estimated equilibrium intensity and I_o the initial intensity. I_{eq} was taken as the mean value of the last few (longest time) data points at 125 and 150 °C and as a point on the straight line shown in (a) at 100 °C. The data are consistent with a rate law of the form $\ln(\Delta Q/\Delta Q_o) \propto t$ at 100 °C. (d) Arrhenius form of a TTT diagram (see Putnis and McConnell, 1980) with data from (b) and (c). Each point represents a single measurement with the observed value of I_k/I_o printed above or below it. The straight lines are only a rough indication of contours of equal I_k/I_o; their slope gives a value of the enthalpy of activation of ~ 70 kJ · mole^{-1}.

what extent the same processes control the development of the incommensurate phases observed in natural minerals remains to be determined.

We suggest that Landau theory for equilibrium behaviour and the Ginzburg–Landau approach to kinetics provide a powerful theoretical and practical basis for assessing the impact of structural phase transitions in minerals on more general geological processes.

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