

Relaxations near surfaces and interfaces for first-, second- and third-neighbour interactions: theory and applications to polytypism

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Abstract. Structural relaxations near surfaces and interfaces are analysed in a simple, generic model with first-, second- and third-layer interactions. The relaxations have exponential envelopes with three types of structural distortion: (i) ferrodistorptive, (ii) antiferrodistorptive, and (iii) modulated (incommensurable). Their stability conditions in the field of control parameters and their relationship with structural phase transitions is derived. A tricritical point is found for three-layer interactions and a transition to an incommensurate phase. All phase transitions to the ferrodistorptive phase are first-order in our model.

The theory is applied to the analysis of lattice relations near internal interfaces in ionic polytypic materials (e.g. PbI_2). Diffuse x-ray scattering and the shift of diffraction angles are the typical fingerprints for such relaxations. The relevant structure factors are calculated. There is tentative agreement between the calculated and observed diffraction profiles.

1. Introduction

Structural phase transitions often generate twin boundaries in the low-symmetry phase. Relaxations of the lattice occur close to such twin boundaries. Similar relaxations can also generate precursor texture in the high-symmetry phase (see Salje (1990, 1991) for a review) whereby the most common relaxations occur near the surface of the crystal. The relevance of this ‘pre-wetting’ phenomenon as precursor effect of the structural phase transition has been discussed in detail by Houchmandzadeh *et al* (1991, 1992). They showed that a particularly stable form of a relaxation near the surface is an oscillation of the order parameter superimposed on an exponential decay. Such a state was called a ‘ripple’. Ripples seem to represent a widespread phenomenon: typical examples include evanescent waves of electronic wavefunctions which were reported as early as 1963 (Heine 1963, 1964). They were also found by computer simulation in alloys (Sutton, 1991) and water–clay interfaces (Skipper *et al* 1991). We show in this paper that ripples, incommensurations etc, do indeed occur for a wide range of control parameters in systems with three interacting layers.

Houchmandzadeh *et al* (1991, 1992) have argued that a quantitative description of twinning and surface relaxations in simple commensurate structures (including ripple

phases) is possible in terms of the Fourier components of two interplanar interactions (first- and second-layer interactions) without further anharmonicities of the interaction potentials. In this paper we show that the generic case contains three interplanar interactions, namely between the first, second and third neighbouring layers. This model allows the description of phase transitions between a high-symmetry phase and commensurate or incommensurate low-symmetry phases and the related lattice relaxations.

Besides the obvious interest of such models for the elucidation of precursor relations and pre-wetting transitions in commensurate and incommensurate phase transitions, we were also motivated to do this study by recent findings on polytypic phase transitions. Polytypism is often related to phase transitions between long-period commensurate structures in layer materials (e.g. Trigunayat 1990). Earlier theoretical work on the origin of polytypism was widely based on the idea that the layer configurations could be mapped onto a spin model of the ANNNI type (see Elliott (1961), Fisher and Selke (1980), Yeomans (1988), see also Selke (1991) for a review). The essential result of these theories was that the various polytypic phases should be stabilized by entropic effects in the domain walls. This prediction was shown to be wrong (at least in the case of non-metallic polytypes) because the related wall instabilities (jogs) do not exist. Furthermore, local structural relaxations in the polytypic layers, especially close to walls, make the definition of a layer-related spin variable meaningless. In an alternative approach, Salje *et al* (1988) presented experimental evidence showing that the stabilization energy of a specific polytype is directly related to its phononic properties. Model calculations and further experimental work by Cheng *et al* (1990) on SiC and Winkler *et al* (1991) on PbI_2 supported this view.

Although the description of polytypism within the phonon-related Landau-type theories, or in the context of the ANNNI model, corresponds to fundamentally different physical mechanisms, there is a formal link between them (Bak and von Boehm 1980). A continuous version of the ANNNI Hamiltonian (review: Selke 1991) including elastic relations can be expected to lead to the same Landau-type expressions as the equivalent 'soft' Ising model in the case of an Ising Hamiltonian with strain-related interactions (Marais *et al* 1991, Salje, 1992, Bratkovsky *et al* 1992).

Having established that models with continuous interlayer interactions are appropriate for the description of polytypism, we can now tackle the main open question in this field, namely that of interfacial relaxations. In order to clarify this problem, let us consider the mechanisms of a polytypic transition as seen, e.g., in PbI_2 (Salje *et al* 1987, Soudmand and Trigunayat 1989). These transitions are discontinuous with nucleation and growth of the stable polytype in a matrix of the unstable polytype. Nucleation often happens near defects or, most commonly, near the surface of the crystal. The growth proceeds layer by layer with rapid expansion of the stable state in each layer. The next layer starts to transform only if the transition has been completed in the previous layer.

In a sideways view of the crystal, the growth of the stable phase occurs like a zig-zag knitting process. Knitting can start simultaneously from various nucleation centres and will ultimately join the transformed parts of the crystal. The essential condition for the reversibility of the transition is now related to the way in which the transformed areas coalesce. If the periodicity is such that the coalescence is without defect (i.e. the polytypic layers meet with the correct stacking sequence) the new phase is uniform and leaves no nucleation centre for the back-transformation. It is

very likely, however, that the transformed areas meet in a stacking sequence which is out of step with the already transformed areas. In this case, a new stacking sequence is locally generated as a 'zip' between the knitted parts. This zip can be opened and closed by changing the control parameters, such as temperature or pressure. In this case, the phase transition is reversible (at least in PbI_2).

The zip represents an internal surface of the crystal surrounded by intense lattice relaxations. These relaxations appear as diffuse x-ray diffraction signals or broadened phonon scattering profiles in Raman spectra (Salje *et al* 1988, Winkler *et al* 1990, Sondmand and Trigunayat 1989). Further indirect evidence stems from structural refinements (Palosz *et al* 1990, Kumar and Trigunayat 1992).

The question now arises: how can we describe these local relaxations (or, indeed, those close to the surface of the crystal) in a simple and self-consistent model? Previously, Parlinski and Michel (1984) have proposed a model for thiourea which included harmonic interactions for distant neighbours augmented by anharmonic couplings. Janssen and co-workers (Janssen and Tjon 1981, 1982, Janssen 1986, Janssen and Janner 1987) have introduced a Hamiltonian with harmonic interactions between first, second and third layers and anharmonic (fourth-order) interactions between neighbouring layers. This model is obviously equivalent to a *soft ANNNI* model (Benkert *et al* 1987).

In this paper, we follow a similar, but even simpler approach and formulate first a model with purely harmonic first- and second-layer interaction (Houchmanzadeh *et al* 1991a) which is then expanded to include the third-layer interaction. We show that this model reproduces the essential experimental observations. Throughout the paper we put emphasis on the close correlation between the phononic and relaxational properties of the phase transition. The paper is organized as follows: the phonon spectra and the phase diagram for two layer interactions are calculated in part 2. In this part we also calculate the relaxation pattern and show that the critical wavevector of the soft mode and the characteristic length of the relaxation can be derived by the same formalism from the characteristic equation of the phonon dispersion.

In part 3 we extend the model to the generic case of three interacting layers (including first-, second- and third-layer interactions). It is shown that incommensurate relaxations now dominate the phase diagram. There is a simple relationship between the relevant wavevectors of the soft modes, the periodicity of the relaxation and its characteristic length. Finally, we calculate the structural factors of the first satellite reflection for a 'realistic' model in part 4 and show that the relaxations lead to asymmetric diffraction profiles with peak positions shifted with respect to the position in the low-symmetry phase. Much of the algebraic treatment is given in the appendix.

2. First- and second-layer interactions

The Hamiltonian of the inter-layer interaction is written in terms of the n th layer coordinate Z_n which may designate a longitudinal coordinate (layer distance $Z_{n+1} - Z_n$) or a transverse coordinate describing the shear of layer $n+1$ with respect to layer n .

The Hamiltonian is

$$H = \sum_n V(Z_{n+1} - Z_n) + V(Z_{n+2} - Z_n). \quad (1)$$

The potential V is kept arbitrary. The equilibrium condition in the bulk of the material is

$$V'(b) + 2V'(2b) = 0 \quad (2)$$

where b is the equilibrium value of Z (e.g. equilibrium distance between layers), V' indicates the first spatial derivative.

We first calculate the phonon spectrum. With the phonon coordinate u_n , we rewrite the layer coordinate Z_n as

$$Z_n = nb + u_n. \quad (3)$$

The difference between the Hamiltonian and its static equilibrium value is

$$H(u) - H(u_0) = \sum_n V(Z_n - Z_{n-1}) + V(Z_n - Z_{n-2}). \quad (4)$$

The second derivative $V''(b) = \phi_1$ and $V''(2b) = \phi_2$ determine the dynamical matrix with

$$\partial^2 Z_n / \partial t^2 = \phi_2(Z_{n+2} + Z_{n-2} - 2Z_n) + \phi_1(Z_{n+1} + Z_{n-1} - 2Z_n). \quad (5)$$

Fourier transform leads to the phonon spectrum

$$\omega^2 = \phi_1 \sin^2(kb/2) + \phi_2 \sin^2(kb) = \sin^2(kb/2)[\phi_1 + 4\phi_2 \cos^2(kb/2)]. \quad (6)$$

The potential parameters appear only in the bracket which we call Ω^2 :

$$\omega^2(k) = \sin^2(kb/2)\Omega^2(k). \quad (7)$$

The stability of phonons requires $\omega^2 \geq 0$ or $\Omega^2(k) \geq 0$ which leads to the conditions for the phase stability

$$\phi_1 \geq 0 \quad (8)$$

$$\phi_1 + 4\phi_2 \geq 0. \quad (9)$$

The equals signs hold for the phase transition in the soft mode limit. The phase transition $\phi_1 \rightarrow 0$ related to a zone-boundary instability (antiferrodistortive transition), the phase boundary $\phi_1 = -4\phi_2$ indicates a Γ -point instability (ferrodistortive transition).

We can now compare these results with the lattice relations close to surfaces or interfaces. Let us consider $Z_{n+1} - Z_n = b + \epsilon_n$ with ϵ_n as the relaxational coordinate. The condition for ϵ_n is $\delta H / \delta \epsilon_n = 0$ which gives $\epsilon_n \neq 0$ only for small values of n and $\epsilon_n = 0$ in the bulk. We find for the first layer in the second-order theory

$$\partial H / \partial \epsilon_0 = V'(2b) + (\phi_1 + \phi_2)\epsilon_0 + \phi_2\epsilon_1 = 0 \quad (10)$$

and for the general n th layer

$$\partial H / \partial \epsilon_n = \phi_2\epsilon_{n-1} + (\phi_1 + 2\phi_2)\epsilon_n + \phi_2\epsilon_{n+1} = 0. \quad (11)$$

Dividing by ϕ_2 , we define the relevant interaction parameter $2\beta = 2 + \phi_1/\phi_2$.

It is shown in appendix 1 that the relaxation amplitude ϵ_n can be expressed using the recursion formula (Houchmandzadeh *et al* 1991)

$$\epsilon_n = \lambda^n \epsilon_0 \quad (12)$$

The characteristic length is determined by $\ln \lambda$ with

$$\lambda_{0,1} = -\beta \pm \sqrt{\beta^2 - 1}. \quad (13)$$

We define as λ_0 the value with $|\lambda_0| \leq 1$. The parameter ϵ_0 is the relaxation of the surface layer

$$\epsilon_0 = (V'(2b)/V''(2b))/[(2\beta - 1) + \lambda_0] \quad \epsilon_1 = \lambda_0 \epsilon_0. \quad (14)$$

These solutions describe three scenarios (figure 1).

(i) An exponential decay of the relaxation occurs for positive values of λ_0 . The largest deformation is in the surface layer. The thickness of the relaxed part of the crystal is $(b \ln \lambda_0)$. The relaxation pattern is characterized by a ferroelastic deformation.

(ii) Zig-zag relaxations with an exponential envelope occur for negative values of λ_0 . The relaxation pattern is similar to that of an antiferroelastic distortion.

(iii) Only uniform states occur for vanishing λ_0 . This value corresponds to $\phi_2 = 0$, i.e. to vanishing interactions between next-nearest layers. No phase transition occurs in this case. Uniform relaxation also exists at the phase-transition point when the correlation length diverges. This case is described by $\lambda = 1$ ($\lambda = -1$) for the ferroelastic (antiferroelastic) phase transition.

In order to pinpoint the close similarity between the phonon softening and the surface relaxation, we formally combine both solutions in one formulation which makes use of the complex completion of the wavevector. Let us start again from the dispersion relation in equation (6). We write this equation in complex notation as

$$\Omega^2 = \phi_1 + 2\phi_2 + \phi_2(e^{ikb} + e^{-ikb}). \quad (15)$$

The exponential terms are identified as $\lambda = \exp(ikb)$. The instability condition that Ω^2 has to vanish has then the same form as the characteristic equation for the relaxational parameter λ in equation (13). As the condition $\Omega^2 = 0$ determines both the length scale of the surface relaxation and the dispersion of the soft mode for the bulk, we can describe both features by one complex relaxation parameter

$$\lambda = \exp(ikb) \text{ with } k = k_R + ik_I. \quad (16)$$

The imaginary part of the wavevector describes the surface relaxation, the real part of the wavevector describes the oscillatory solution which exists only in the bulk. The complex dispersion relation is now

$$\Omega^2 = \phi_1 + 2\phi_2 + \phi_2(\exp(ik_R b) \exp(-k_I b) + \exp(-ik_R b) \exp(k_I b)). \quad (17)$$

The condition $\Omega^2 = 0$ leads again to

$$\lambda^2 + 2\beta\lambda + 1 = 0. \quad (18)$$

All solutions for λ are real because $\beta^2 > 1$ in the high-symmetry phase. This leads immediately to $\exp(ik_R b) = 1$ with the two solutions $k_R = 0$ and $k_R = \pi/b$ for the soft modes at the zone centre and zone boundary, respectively. The relaxational part has the wavevector $k_I = -(\ln \lambda)/b$ which vanishes at the point of the phase transition along one of the two possible trajectories where k_R is a constant (namely 0 or π/b).

3. Three interacting layers

The model of first and second interacting layers is now extended to include a third-nearest neighbour. We shall show that the degeneracy of the phase diagram for two layers at $\phi_2 = 0$ is lifted. As a consequence we find the appearance of incommensurations and equivalent relaxations. The Hamiltonian is now

$$H = \sum V(Z_{n+1} + Z_n) + V(Z_{n+2} - Z_n) + V(Z_{n+3} - Z_n) \quad (19)$$

with the equilibrium condition

$$V'(b) + 2V'(2b) + 3V'(3b) = 0. \quad (20)$$

The phonon dispersion follows in strict analogy with the previously discussed scenario as

$$\omega^2(k) = \sin^2(kb/2)\Omega^2(k) \quad (21)$$

$$\Omega^2 = (\phi_1 + 2\phi_2 + 3\phi_3) + 2(\phi_2 + 2\phi_3) \cos kb + 2\phi_3 \cos^2 kb \quad (22)$$

that is

$$\Omega^2 = \phi_1 + 4\phi_2 + 9\phi_3 - 4(\phi_2 + 6\phi_3) \sin^2(kb/2) + 16\phi_3 \sin^4(kb/2). \quad (23)$$

Stable solutions ($\Omega^2 > 0$) exist for

$$\phi_1 + 4\phi_2 + 9\phi_3 > 0 \quad (k = 0) \quad (24)$$

$$\phi_1 + \phi_3 > 0 \quad (k = \pi/b) \quad (25)$$

$$-6 < \frac{\phi_2}{\phi_3} < 2 \text{ or } \phi_2^2 < 4\phi_3(\phi_1 + \phi_2) \quad \text{incommensurate.} \quad (26)$$

These conditions define the phase diagram in figure 2. Comparing figure 2 with figure 1 one finds that the role of ϕ_3 is to shift the phase boundaries for the zone-centre and zone-boundary transition thereby increasing the stability field of the high-symmetry phase for $\phi_3 > 0$. The second effect is to split the degeneracy line $\phi_2 = 0$ into a parabola which is asymptotic to the two first phase boundaries at the points A and B. Along the segment A-B the $\Omega = 0$ condensation occurs between the $k = 0$ and $k = \pi/b$ limits, leading to incommensurations and long-period structures. The extent of this segment is proportional to ϕ_3 .

The relaxational pattern follows from the minimization of H with respect to the three parameters ϵ_0 , ϵ_1 and ϵ_2 with

$$\partial H / \partial \epsilon_0 = (\phi_1 + \phi_2 + \phi_3)\epsilon_0 + (\phi_2 + \phi_3)\epsilon_1 + \phi_3\epsilon_2 - V'(2b) - 2V'(3b) = 0 \quad (27)$$

$$\partial H / \partial \epsilon_1 = (\phi_2 + \phi_3)\epsilon_0 + (\phi_1 + 2\phi_2 + 2\phi_3)\epsilon_1 + (\phi_2 + 2\phi_3)\epsilon_2 + \phi_3\epsilon_3 - V'(3b) = 0 \quad (28)$$

$$\begin{aligned} \partial H / \partial \epsilon_n &= \phi_3\epsilon_{n-2} + (\phi_2 + 2\phi_3)\epsilon_{n-1} + (\phi_1 + 2\phi_2 + 3\phi_3)\epsilon_n + (\phi_2 + 2\phi_3)\epsilon_{n+1} \\ &+ \phi_3\epsilon_{n+2} = 0 \quad \forall n > 1. \end{aligned} \quad (29)$$

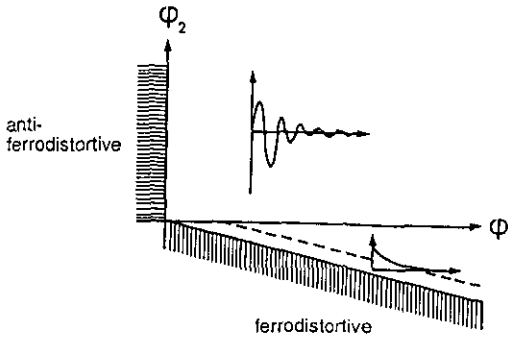


Figure 1. Phase diagram for a system with two-layer interactions. (Potential parameter ϕ_1 between nearest layers and ϕ_2 between next-nearest layers.) The solid lines indicate the marginal stability of the high-symmetry phase. Due to third-order terms, the transition to the ferrodistortive phase is first-order for conditions as indicated by the dashed line. Surface relaxations oscillate for $\phi_2 > 0$ and decay purely exponentially for $\phi_2 < 0$.

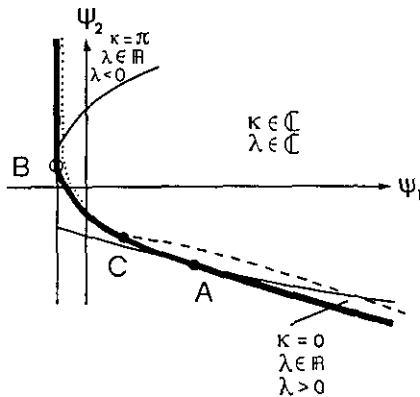


Figure 2. Phase diagram for a system with three-layer interactions (first neighbour ϕ_1 , second neighbour ϕ_2 , third neighbour ϕ_3 , $\Psi_1 = \phi_1/\phi_2$, $\Psi_2 = \phi_2/\phi_3$). The thick line indicates the loci of the marginal stability of the paraphase with antiferro-states for Ψ_2 greater than at point B, incommensurations between A and B and ferro-states at Ψ_1 greater than at point A. The phase transitions to the ferro-state are always first-order with the loci of the transition indicated by the dashed line. The point C represents a tricritical transition with second-order transitions to the incommensurate phase between C and B. For Ψ_1 slightly greater than at the point C, the transition is also an incommensurate phase but first-order, as in the case of the transition to the ferrophase. The dotted line shows the new 'pre-wetting' transition of the transverse relaxation. Surface relaxations are exponential in the small area ($k = 0$) at large Ψ_1 -values, commensurate (zone-boundary) relaxations ($k = \pi$) at Ψ_2 greater and incommensurate inside the parabola ($\frac{1}{4}\Psi_2^2 - (\Psi_1 + \Psi_2) = 0$).

The analytical treatment is given in appendix 2. It is shown then that the solution which is compatible with the boundary condition $\epsilon_n = 0$ for $n = \infty$ can be written as two decay functions

$$\epsilon_n = p\lambda_1^n + q\lambda_2^n \tag{30}$$

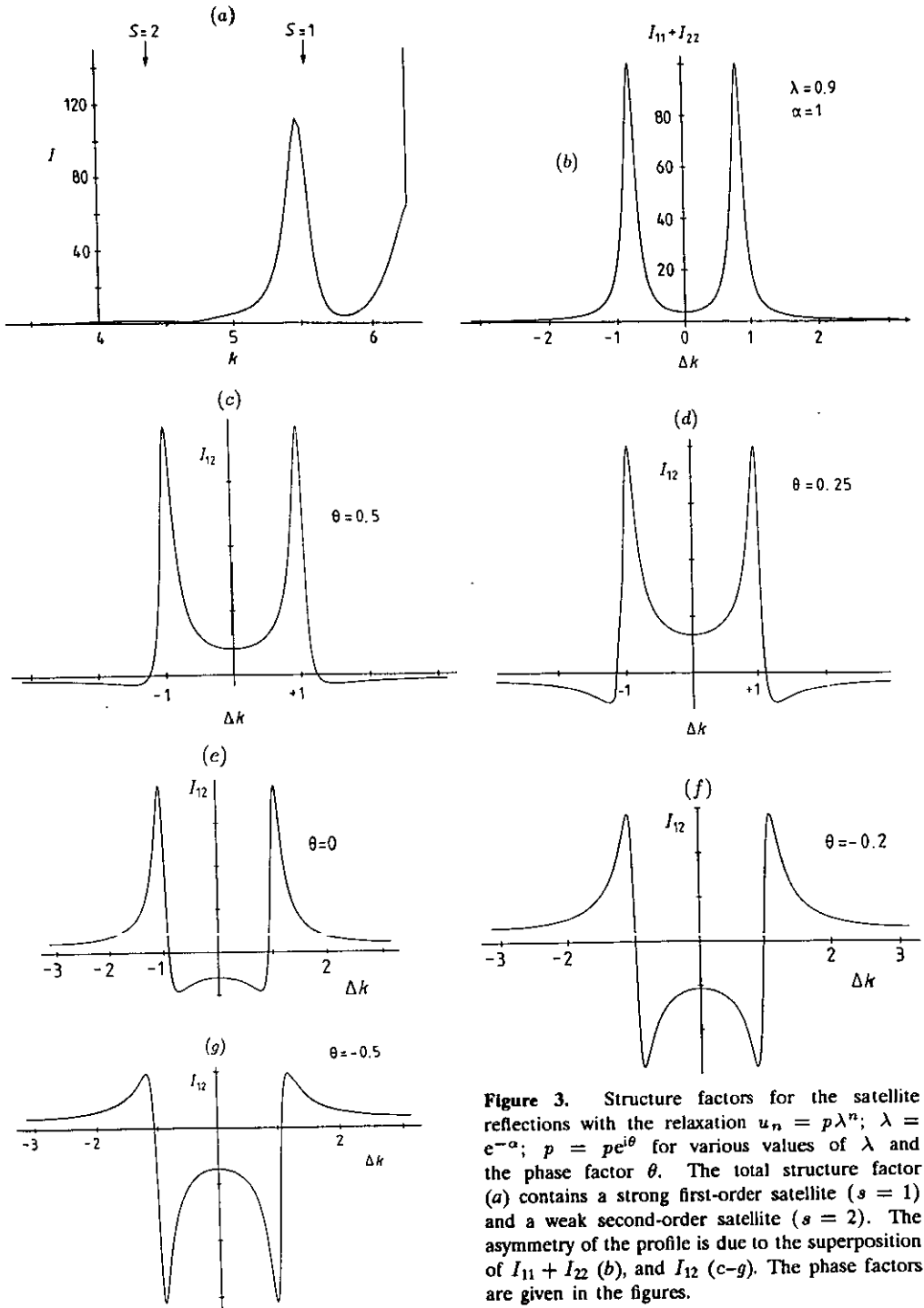


Figure 3. Structure factors for the satellite reflections with the relaxation $u_n = p\lambda^n$; $\lambda = e^{-\alpha}$; $p = pe^{i\theta}$ for various values of λ and the phase factor θ . The total structure factor (a) contains a strong first-order satellite ($s = 1$) and a weak second-order satellite ($s = 2$). The asymmetry of the profile is due to the superposition of $I_{11} + I_{22}$ (b), and I_{12} (c-g). The phase factors are given in the figures.

where p and q are constant amplitudes determined by the potential parameters (appendix 2). The relaxation depends now, in the most general case, on two

relaxational parameters λ_1 and λ_2 and, thus, on two length scales. The values of λ are determined by the characteristic equation

$$\lambda^4 + 2(1 + \phi_2/2\phi_3)\lambda^3 + (3 + (\phi_1 + 2\phi_2)/\phi_3)\lambda_2 + 2(1 + \phi_2/2\phi_3)\lambda + 1 = 0. \quad (31)$$

We now allow again the wavevector to be a complex number $k = k_R + ik_I$ and find with $\lambda = \exp(ikb)$ that there are four solutions with $\lambda_1\lambda_3 = 1$ and $\lambda_2\lambda_4 = 1$. Only the two solutions with $|\lambda_m| < 1$ fulfil our boundary condition that the relaxation has to vanish for large distances from the surface or interface. Let us call these two solutions λ_1 and λ_2 . If λ_m is a complex number, we find that λ_m^* is also a solution because all coefficients of the characteristic equations are real numbers.

After we have derived the phonon instabilities and the surface relaxations separately, let us now show that both solutions can be related directly to the phonon dispersion in equation (23). We use again the same *ansatz* $\lambda = \exp(ikb)$ where the wavevector k is a complex number. The dispersion relation is then

$$\begin{aligned} \Omega^2(k) = & (\phi_1 + 2\phi_2 + 3\phi_3) + 2(\phi_2 + 2\phi_3) \cos(k_R b) \cosh(k_I b) \\ & + 2\phi_3 \cos(2k_R b) \cosh(2k_I b) + i[2(\phi_2 + \phi_3) \sin(k_R b) \sinh(k_I b) \\ & + 2\phi_3 \sin(2k_R b) \sinh(k_I b)]. \end{aligned} \quad (32)$$

We now explore the instabilities in the same way as in the case of two interacting layers, namely the condition $\Omega^2 = 0$. There are three types of solution

$$(i) \quad k_R = 0 \quad k_1^{(1)} = -(\ln \lambda_1)/b \quad k_1^{(2)} = -(\ln \lambda_2)/b \quad (33)$$

$$(ii) \quad k_R = \pi/b \quad k_1^{(1)} = -(\ln \lambda_1)/b \quad k_1^{(2)} = -(\ln \lambda_2)/b \quad (34)$$

$$(iii) \quad 0 < k_R < \pi/b \quad k_1^{(1)} = -k_1^{(2)}. \quad (35)$$

Solutions (i) and (ii) describe uniform relaxation (1) or zig-zag relaxation (2) with two characteristic length scales each. It is only the appearance of the second length scale which distinguishes the behaviour of three interacting layers from that of two interacting layers. The fundamentally new case is solution (iii) with only one characteristic length of relaxation but a continuously variable wavevector for the modulation. The structural state is that of an exponentially decaying incommensurate phase attached to the surface or interface.

The relaxation disappears if these solutions degenerate (modulo the phase angle), which means $|\lambda| = 1$. This defines the condition that the structural phase transition takes place in the bulk. For $\lambda = 1$ the Γ -point transition takes place, for $\lambda = i$ the low-symmetry phase condenses at the zone boundary and for all other $|\lambda| = 1$ the low-symmetry phase is modulated (commensurably or incommensurably).

A second singularity, albeit not always a phase transition, occurs when $4\phi_3(\phi_1 + \phi_2) = \phi_2^2$. Under this condition regimes (i) and (iii) or (ii) and (iii) join and the degeneracy of k increases. The real parts of the two k -vectors of λ_1 and λ_2 disappear simultaneously leaving no long-wavelength oscillations. The two equivalent imaginary parts become identical and there is, thus, only one length scale in the relaxation as in the case of only two-layer interactions.

4. On the longitudinal and transverse character of the relaxation

Let us now discuss some specific features of the phase diagram in figure 2 and the physical nature of the relaxation. So far we have tacitly assumed that all relaxations are longitudinal in character, i.e. the interlayer spacings change when they approach the surface or interface. This type of relaxation does always exist and there is no symmetry restriction which confines the relaxation amplitudes. This means that the first derivatives of the potential in equations (27) and (28) (but not in equation (29)) have finite values and constitute the conjugate surface field in the traditional Landau theory. These terms are responsible for the first-order character of the transition between the paraphase and the ferrodistorptive phase or some incommensurate phases.

Besides the longitudinal relaxations, there exist also transverse relaxations for which the lattice planes are sheared against each other. In case of polytypic phase transitions, they are responsible for the fact that new phases grow from the surface or from interfaces. The essential difference between the longitudinal and transverse relaxation is that the latter breaks the symmetry of the paraphase. In the paraphase, a shear of the surface layers to the 'right' is equivalent to a shear to the 'left'. This requires that the field terms in the equations (27) and 28 disappear identically (which will occur only for specific surfaces and interfaces) otherwise the treatment of transverse and longitudinal relaxations is strictly identical. It is now easy to show that the Gibbs free energy of the surface relaxation is a Landau-type polynomial of the two amplitudes of the decay functions p and q (equation (30)) including a bilinear coupling term pq . This means that only two solutions exist, namely

$$p = q = 0 \quad \text{and} \quad p \neq 0, q \neq 0$$

but never

$$p = 0, q \neq 0 \quad \text{or} \quad p \neq 0, q = 0.$$

The first allowed solution represents the state of no transverse surface relaxation, the second that with the surface relaxation. Between both states we find a phase transition closely associated to a pre-wetting transition (dotted line in figure 2).

We have seen so far that longitudinal relaxations always exist for all surfaces and interfaces. They represent one of the most common precursor effects of the phase transition. In contrast to the longitudinal relaxations, transverse relaxations exist only for specific surfaces and interfaces. They break the local symmetry and give rise to an additional phase transition. This analysis now clearly provokes a number of new questions. One of the most fascinating questions relates to relaxations near vicinal surfaces and rough surfaces. In the first case, a specific surface with transverse relaxations is tilted by a small angle so that periodic kinks appear in the surface. These kinks break the same symmetry locally, as does the transverse relaxation during the 'pre-wetting' transition. Such a situation allows the study of a phase transition with strictly periodic, symmetry-breaking fields.

The second type of question relates to rough surfaces. Again, the roughness acts as a symmetry-breaking field which is now random. Rough surfaces or rough interfaces provide an almost ideal source of a random field acting on the pre-wetting order parameter. As the roughening transition may occur at higher temperatures than the polytypic or ferroelastic phase transition, one can image a situation in which the surface relaxation can be investigated for different control parameters and for well defined amplitudes of the random field. Such investigations are planned for further work.

5. Structure factor

The most obvious indication for strong lattice relaxations is the experimental observation that superlattice diffraction signals are streaked and arched (e.g. Sondmand and Trigunayat 1989). Furthermore, their maximum intensity is not located at the equivalent diffraction angle for the ideal structure but slightly shifted (Salje *et al* 1987). Trigunayat (1966) related the streaking to the formation of structural disorder near the polytypic interfaces (i.e. the zips). The arches were related to the movement of dislocations into small-angle boundaries. Although these topological lattice imperfections are expected to carry the main part of the diffraction intensities outside the Bragg reflections of the perfect lattice, it appears that our model explains similar effects simply as the result of the intrinsic lattice relaxation near the surface and the interfaces. In particular the asymmetry of the scattering profile of the superlattice reflections can easily be derived from the shape of the lattice relaxation (*without* the evocation of any topological disorder!). In order to illustrate this argument, let us consider an orthogonal system. The reduced structure factor $A'(hk)$ in the plane perpendicular to the surface or interface (appendix 3) is for the first satellite reflection

$$A'(hk) = \sum_{s=0}^{\infty} \sum_{t=0}^s (ik)^s \binom{s}{t} \frac{p^t q^{s-t}}{s!} \sum_{m=0}^{\infty} \exp(imha - mt\alpha_1 - m(s-t)\alpha_2) \quad (36)$$

which includes the exponential relaxation with

$$u_n = p\lambda_1^n + q\lambda_2^n \quad \lambda = \exp(-\alpha). \quad (37)$$

The intensity for $s = 0$ yields the same δ -reflections as the original lattice. The relaxations lead to satellite peaks with $s = 1$ with

$$A'(h, k) = \sum_{s=0}^{\infty} J(s) \quad (38)$$

$$J(1) = ikp \sum_{m=0}^{\infty} \exp(imha - m\alpha_1) + ikq \sum_{m=0}^{\infty} \exp(imha - m\alpha_2). \quad (39)$$

Only cases with $|\lambda| \neq 1$ lead to exponential relaxations so that $\text{Re}(\alpha) \neq 0$. This part leads to a simple geometrical series in m with the value

$$J(1) = ik [p/[1 - \exp(iha - \alpha_1)] + q/[1 - \exp(iha - \alpha_2)]]. \quad (40)$$

In the case of an incommensurate relaxation with

$$\lambda_1 = \lambda_2^* \quad \alpha_1 = \alpha_2 \quad p = q^* \quad (41)$$

we consider the real and imaginary part of α separately and find

$$\alpha_1 = \alpha' + i\alpha'' \quad \alpha_2 = \alpha' - i\alpha'' \quad p = p_0 e^{i\theta} \quad q = p_0 e^{-i\theta}. \quad (42)$$

The reduced structure factor then becomes

$$J(1) = ikp_0 \left[\frac{e^{i\theta}}{1 - \exp(i(ha - \alpha'') - \alpha')} + \frac{e^{-i\theta}}{1 - \exp(i(ha + \alpha'') - \alpha')} \right]. \quad (43)$$

The diffraction profile follows from the square of the structure factor and is proportional to three contributions:

$$I(1) = k^2 p_0^2 (I_{11} + I_{22} + I_{12}) \quad (44)$$

where

$$I_{11} = (1 - 2|\lambda| \cos(ha - \alpha'') + |\lambda|^2)^{-1} \quad I_{22} = (1 - 2|\lambda| \cos(ha + \alpha'') + |\lambda|^2)^{-1} \quad (45)$$

are the diagonal terms and

$$I_{12} = \{\cos 2\theta + |\lambda|^2 \cos(2\theta + \alpha'') - 2\cosh a \cos(2\theta + \alpha'')\} / [(1 + |\lambda|^2)^2 + 2|\lambda|^2(\cos 2ha + \cos 2\alpha'') - 4\cosh a \cos \alpha''(|\lambda| + |\lambda|^3)] \quad (46)$$

describes the mixing of the two decays.

The profiles I_{11} and I_{22} give two symmetrical peaks at $h \pm \alpha''/a$, i.e. the superlattice reflections. These reflections do not necessarily correspond to the final reflections of the low-symmetry form because α'' changes as a function of the control parameter. The cross term I_{12} is asymmetric and leads to additional weak scattering.

We now calculate the scattering profiles for 'reasonable' model parameters. With $\alpha'' = 1$ and $\lambda = 0.9$ we find the two satellite reflections $I_{11} + I_{22}$ in figure 4. For the cross term $I_{12}(h)$, the intensity also depends on the phase angle θ . In figure 4 the results for various angles between $\pi/4$ and 0 are shown. We then compare the results of the analytical calculations for a model with $p = 0.5 \exp(-i/2)$ and $\lambda = 0.9 \exp(0.8i)$ with those of computer simulations on a chain of 200 atoms. The final results are shown in figure 4 showing a weakly asymmetric peak profile with a maximum shifted as a function of the control parameter. This peak profile agrees, at least quantitatively, with the observed asymmetry of the diffraction profiles in PbI_2 and the shift of the peak position when the transition point is approached in polytypic transformation. A more quantitative comparison is not yet possible, however, because the analysis of the experimental profiles is hampered by additional effects due to other lattice imperfections in the as-grown material. Further studies of other polytypic material, such as SiC, for the analysis of the fine structure of the diffraction profiles are planned.

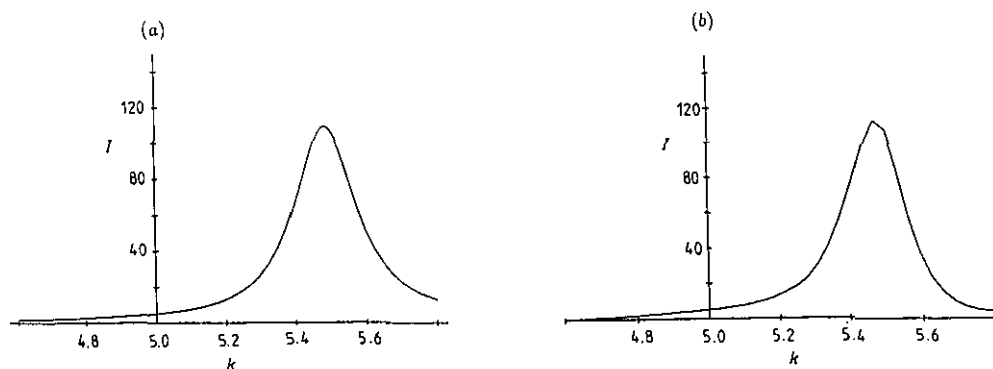


Figure 4. Analytical structure factor (a) and the result of computer simulation (b) with $u_0 = 0.5 \exp(0.5i)$, $\lambda = 0.9 \exp(0.8i)$.

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Appendix 1

The regression relation for two interacting layers in equations (10) and (11) can be written in matrix form

$$\begin{pmatrix} \epsilon_{i+1} \\ \epsilon_i \end{pmatrix} = \mathbf{B}^i \begin{pmatrix} \epsilon_1 \\ \epsilon_0 \end{pmatrix} \quad (\text{A1})$$

where the transfer matrix $\mathbf{B} = \begin{pmatrix} -2\beta & -1 \\ -1 & 0 \end{pmatrix}$ is the standard map of the non-linear equation (11). The relaxation is due to the non-diagonal form of \mathbf{B} . In the eigensystem, \mathbf{B} can be diagonalized with

$$\mathbf{B}' = \begin{pmatrix} \lambda_0 & 0 \\ 0 & \lambda_1 \end{pmatrix} \quad (\text{A2})$$

where λ_0, λ_1 are the solutions of the characteristic equation $\lambda^2 + 2\beta\lambda + 1 = 0$, or

$$\lambda_{0,1} = -\beta \pm \sqrt{\beta^2 - 1} \quad (\text{A3})$$

and

$$\lambda_0 \lambda_1 = 1. \quad (\text{A4})$$

The transformation matrix between the non-diagonal and the diagonal basis is \mathbf{P} with $\mathbf{B}^n = \mathbf{P}(\mathbf{B}')^n \mathbf{P}^{-1}$ and

$$\mathbf{P} = \begin{pmatrix} 1 & 1 \\ \lambda_1 & \lambda_0 \end{pmatrix} \quad \mathbf{P}^{-1} = \frac{1}{\lambda_0 - \lambda_1} \begin{pmatrix} \lambda_0 & -1 \\ -\lambda_1 & 1 \end{pmatrix}. \quad (\text{A5})$$

The eigenvalue of ϵ_n is then

$$\epsilon_n = [1/(\lambda_0 - \lambda_1)][(\lambda_0^n - \lambda_1^n)\epsilon_1 - (\lambda_0^{n-1} - \lambda_1^{n-1})\epsilon_0] \quad (\text{A6})$$

and depends only on $\lambda_{0,1}$, and the initial values of ϵ_n and ϵ_0 close to the surface. In the bulk, we required $\epsilon_n \rightarrow 0$ for $n \rightarrow \infty$ which is only possible for $|\lambda_1| > 1$ if $\lambda_1 \epsilon_1 - \epsilon_0 = 0$.

This convergence condition and the equilibrium condition for the first layer (equation (10)) determine the values of ϵ_0 and ϵ_1 as

$$\epsilon_0 = (V'(2b)/V''(2b))/[(2\beta - 1) + \lambda_0] \quad \epsilon_1 = \lambda_0 \epsilon_0. \quad (\text{A7})$$

Replacing ϵ_1 by ϵ_0 in equation (A 6) leads to the final recursion formula as already used by Houchmanzadeh *et al* (1991):

$$\epsilon_n = \lambda_0^n \epsilon_0. \quad (\text{A8})$$

Appendix 2

The relaxation equations (27)–(29) are reformulated using the transfer matrix

$$\mathbf{B} = \begin{pmatrix} -2\alpha & -\beta & -2\alpha & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{A9}$$

where

$$\alpha = 1 + \phi_2/(2\phi_3) \quad \beta = 3 + (\phi_1 + 2\phi_2)/\phi_3. \tag{A10}$$

The transfer matrix can now be diagonalized with the eigenvalues given as the solution of the characteristic equation

$$\lambda^4 + 2\alpha\lambda^3 + \beta\lambda^2 + 2\alpha\lambda + 1 = 0 \tag{A11}$$

as

$$2\lambda_{1,3} = -(\alpha - \Delta) \pm \sqrt{(\alpha - \Delta)^2 - 4} \quad \lambda_1\lambda_3 = 1 \tag{A12}$$

$$2\lambda_{2,4} = -(\alpha + \Delta) \pm \sqrt{(\alpha + \Delta)^2 - 4} \quad \lambda_2\lambda_4 = 1 \tag{A13}$$

$$\Delta = \sqrt{\alpha^2 - \beta^2 + 2} \tag{A14}$$

We find two pairs of conjugate eigenvalues λ_0 and λ_1 , and λ_2 and λ_3 . The transformation matrix \mathbf{P} is

$$\mathbf{P} = \begin{pmatrix} \lambda_1^3 & \lambda_2^3 & \lambda_3^3 & \lambda_4^3 \\ \lambda_1^2 & \lambda_2^2 & \lambda_3^2 & \lambda_4^2 \\ \lambda_1 & \lambda_2 & \lambda_3 & \lambda_4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \tag{A15}$$

the n th relaxation parameter ϵ_n follows then from

$$\epsilon_n = \sum_{k,l=1}^4 g_{k,l} \lambda_k^n \epsilon_{l-1} \tag{A16}$$

with the coefficients $g_{k,l}$ defined by \mathbf{P} as

$$g_{k,1} = 1/f \quad g_{k,2} = -\sum_{j \neq k} \lambda_j / f \quad g_{k,3} = \sum_{j \neq k \neq i} \lambda_j \lambda_i / f \tag{A17}$$

$$g_{k,4} = \lambda_i \lambda_j \lambda_l / f \quad i \neq j \neq l \neq k \quad f = \lambda^4 + 2\alpha\lambda^3 + \beta\lambda^2 + 2\alpha\lambda + 1. \tag{A18}$$

We can again choose one of the conjugate λ -values to be greater than unity. With the choices $|\lambda_1| > 1$ and $|\lambda_3| > 1$, the condition for ϵ_n becomes

$$g_{1,1}\epsilon_1 + g_{1,2}\epsilon_2 + g_{1,3}\epsilon_3 + g_{1,4}\epsilon_4 = 0 \tag{A19}$$

$$g_{3,1}\epsilon_1 + g_{3,2}\epsilon_2 + g_{3,3}\epsilon_3 + g_{3,4}\epsilon_4 = 0 \tag{A20}$$

which determines the full set $\{\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3\}$. The relaxation amplitude is then

$$\epsilon_n = p\lambda_1^n + q\lambda_2^n \tag{A21}$$

with

$$p = [-\gamma_1 f(\lambda_2) + \gamma_2 g(\lambda_2)]/\Delta \quad (\text{A22})$$

$$q = [+ \gamma_1 f(\lambda_1) - \gamma_2 g(\lambda_1)]/\Delta \quad (\text{A23})$$

$$\epsilon_0 = p + q \quad (\text{A24})$$

where

$$\Delta = f(\lambda_1)g(\lambda_2) - f(\lambda_2)g(\lambda_1) \quad (\text{A25})$$

$$f(\lambda) = (1 + \phi_2/\phi_3) + (2 + 2\phi_2/\phi_3 + \phi_1/\phi_3)\lambda + (2 + \phi_2/\phi_3)\lambda^2 + \lambda^3 \quad (\text{A26})$$

$$g(\lambda) = (1 + \phi_1/\phi_3 + \phi_2/\phi_3) + (1 + \phi_2/\phi_3)\lambda + \lambda^2. \quad (\text{A27})$$

It is now easy to show that the two leading terms of the Gibbs free energy in ϵ_0 are

$$G = -\gamma\zeta_2\epsilon_0 + [\zeta_1/(1 + \lambda)]\epsilon_0^2/2 + \dots \quad (\text{A28})$$

for the case of longitudinal relaxations. The term

$$\gamma\zeta_2 = \zeta_2 \sqrt{\phi_2^2/4\phi_3^2 - \phi_2/\phi_3 - \phi_1/\phi_3}$$

is the equivalent of the conjugated field H in Landau theory whereby H is created by the surface. It is obvious from symmetry arguments that H can only exist for longitudinal relaxations whereas transverse relaxations require $H = 0$.

Appendix 1. The derivation of the reduced structure factor

The lattice points are described by

$$\mathbf{r}_{m,n,p} = ma\mathbf{e}_x + nb\mathbf{e}_y + pc\mathbf{e}_z \quad (\text{A29})$$

and the diffraction vector is

$$\mathbf{k} = h\mathbf{e}_x + k\mathbf{e}_y + l\mathbf{e}_z. \quad (\text{A30})$$

The displacement vector with respect to the paraphase is

$$\mathbf{u} = (pe^{-mK_1} + qe^{-mK_2})\mathbf{e}_y \quad (\text{A31})$$

for a deformation along the crystallographic y -axis. The intensity of the superlattice reflection is

$$I(\mathbf{k}) = C|A(\mathbf{k})|^2 \quad (\text{A32})$$

with the structure factor $A(\mathbf{k})$, which becomes

$$A(hkl) = \left(\sum \delta \left(k - \frac{2\pi h}{b} \right) \right) \left(\sum \delta \left(1 - \frac{2\pi h}{c} \right) \right) A'(hk) \quad (\text{A33})$$

where the δ -function applies to the ideal, infinite crystal. The reduced structure factor is

$$A'(hk) = \sum_{s=0}^{\infty} \sum_{t=0}^s (ik)^s \binom{s}{t} \frac{p^t q^{s-t}}{s!} \sum_{m=0}^{\infty} \exp\{imha - m\alpha_1 t - m\alpha_2(s-t)\}. \quad (\text{A34})$$

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