

Finite strain Landau theory of high pressure phase transformations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 275202

(<http://iopscience.iop.org/0953-8984/19/27/275202>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 19:37

Please note that [terms and conditions apply](#).

Finite strain Landau theory of high pressure phase transformations

W Schranz¹, A Tröster¹, J Koppensteiner¹ and R Miletich²

¹ Faculty of Physics, University of Vienna, Boltzmannngasse 5, A-1090 Wien, Austria

² Mineralogisches Institut, Universität Heidelberg, Im Neuenheimer Feld 236, 69120 Heidelberg, Germany

E-mail: wilfried.schranz@univie.ac.at

Received 18 December 2006, in final form 9 March 2007

Published 1 June 2007

Online at stacks.iop.org/JPhysCM/19/275202

Abstract

The properties of materials near structural phase transitions are often successfully described in the framework of Landau theory. While the focus is usually on phase transitions, which are induced by temperature changes approaching a critical temperature T_c , here we will discuss structural phase transformations driven by high hydrostatic pressure, as they are of major importance for understanding processes in the interior of the earth. Since at very high pressures the deformations of a material are generally very large, one needs to apply a fully nonlinear description taking physical as well as geometrical nonlinearities (finite strains) into account. In particular it is necessary to retune conventional Landau theory to describe such phase transitions. In Tröster *et al* (2002 *Phys. Rev. Lett.* **88** 55503) we constructed a Landau-type free energy based on an order parameter part, an order parameter–(finite)strain coupling and a nonlinear elastic term. This model provides an excellent and efficient framework for the systematic study of phase transformations for a wide range of materials up to ultrahigh pressures.

We illustrate the model with the specific example of $\text{BaCr}(\text{Si}_4\text{O}_{10})$, showing that it fully accounts for the elastic softening which is observed near the pressure induced phase transformation.

1. Introduction

A major achievement of Ekhard Salje and co-workers was to show that Landau theory can be very efficiently applied to the description of experimental data near temperature induced structural phase transitions in minerals (Salje 1990, 1992, Carpenter *et al* 1998). There are a couple of reasons for this success. First of all, as coupling to strains induces long range forces and enhances anisotropy, strain-induced interactions always tend to suppress fluctuations, leading to a mean field type transition (Bratkovky *et al* 1995). Depending on the nature of the

system (i.e. on the type of coupling between the strain and order parameter, its anisotropy and the boundary conditions imposed on its surface) strain effects may also change the character of the transition from second to first order (Bergman and Halperin 1976). In principle, a Landau potential can be obtained from a low order Taylor expansion of the mean field free energy (e.g. Parlinski *et al* 1989). The problem of how to determine the range of validity of this expansion naturally arises. To answer this question one observes that in many mineral systems the phase transitions turn out to be of the displacive type (Dove 1997). For such systems, the above authors were able to show that Landau theory indeed allows us to reproduce experimental data in an extremely broad temperature range, in particular down to very low temperatures, by taking into account the effect of quantum saturation (Salje *et al* 1991). The situation is not so simple for the other extreme, i.e. order–disorder phase transitions, since it is no longer possible to approximate their free energy by a low order polynomial in the order parameter (Giddy *et al* 1989). In passing, we note that real systems are often of mixed, i.e. displacive/order–disorder character (Meyer *et al* 2000, Sondergeld *et al* 2000), and the characterization of crossover systems in between a displacive and order–disorder type is still a matter of active research (Pérez-Mato *et al* 2000, Rubtsov *et al* 2000, Tröster *et al* 2005).

In ‘traditional’ Landau theory it is difficult to include pressure effects beyond the infinitesimal strain approximation. Therefore one frequently resorts to replacing the elastic background energy by its harmonic truncation and consequently treats the strains as infinitesimal. Since the total strains appearing in temperature induced phase transitions are as a rule quite small this is well justified. However, when we discuss the role of extremely high pressure in driving the transition, the validity of this assumption must be seriously doubted.

At high pressure a phase transition is usually detected by anomalies, for example in the system volume $V(P)$, which in turn result from anomalies in the pressure dependence of the lattice parameters $a_i(P)$, $i = 1, 2, 3$, near a critical pressure P_c . In many cases this leads to an additional (with respect to the ‘background’) nonlinear P dependence of lattice parameters and/or volume. As a function of pressure, the ‘stiffness’ of any solid is characterized by the isothermal compressibility $\kappa(P) = -d \log V(P)/dP$. Various theoretical concepts are usually employed to derive so-called equations of state (EOS) (Anderson 1995, Angel 2000a, 2000b), which—in the absence of phase transitions—describe the hydrostatic pressure dependence of the crystal’s volume $V(P)$.

In the presence of a high pressure phase transition (HPPT) a commonly adopted practice is to merely fit the corresponding $V(P)$ behaviour to a number of differently parametrized EOS for each phase (Schulte and Holzapfel 1995, Krüger and Holzapfel 1992, Chesnut and Vohra 2000), and, apart from computer simulations, in the case of a reconstructive phase transition there is little more one can do at present. However, from a theoretical point of view, although this purely phenomenological procedure does fit experimental volume data in many cases, it neither describes the pressure behaviour of individual strain components nor provides any possible further insight into the mechanisms of a HPPT. A more profound theoretical approach is therefore of vital interest to a broad audience encompassing physicists studying the high pressure behaviour of materials (crystals, liquid crystals, complex liquids, biological membranes, etc) to geologists investigating the earth’s minerals and bulk properties.

Indeed, for HPPTs of the group–subgroup type, it is natural to expect that one could do much better by applying the concepts of Landau theory. In particular, we should be able to connect the high and low pressure phase by a *uniform* thermodynamic description. However, here one faces a marked difference compared to the temperature driven case. At high pressures, as the inter-atomic forces opposing further compression, a crystal’s volume and lattice parameters develop large strains in a pronounced nonlinear way, which corrupts any serious attempt to treat the elastic energy in the framework of the infinitesimal strain

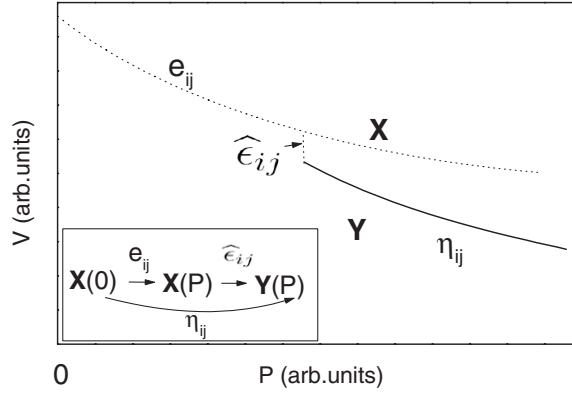


Figure 1. Sketch of deformation states and superposition of strains.

approximation. For these reasons it is necessary to reconsider the construction of Landau theory at extremely high pressures and large deformations (Tröster *et al* 2002). Here we summarize the main ideas of this new theoretical approach and discuss some consequences for the elastic behaviour of materials.

2. New approach for high pressure phase transformations

As stated above, the conventional infinitesimal strain approach is clearly insufficient for achieving an accurate description of HPPTs. Instead, at high pressures the elastic response of a system must be characterized in terms of an appropriate nonlinear strain measure like the Lagrangian or Eulerian strain tensor. Let \mathbf{X} and \mathbf{X}' denote an undeformed reference system and a deformed system, respectively. Then, from the deformation gradient tensor $\alpha_{ik} = \partial X'_i / \partial X_k$ one constructs the Lagrangian strain tensor $e_{ik} = \frac{1}{2} (\sum_n \alpha_{ni} \alpha_{nk} - \delta_{ik})$. In the present work, we consider three such pairs of coordinate systems, which serve as reference systems for measuring the following strains (cf figure 1). For measuring the ‘background strain’ $e(P)$, which is defined as the Lagrangian strain displayed by the system at the constraint of zero order parameter \bar{Q} (see below), $\mathbf{X}(P)$ denotes the corresponding state and $\mathbf{X}(P=0)$ is used as a reference system. For measuring the spontaneous strain $\hat{\epsilon}$ resulting from the emergence of $\bar{Q} \neq 0$, $\mathbf{X}(P)$ plays the role of a (hypothetical) ‘floating’ background reference system. Above the critical pressure P_c , the total strain $\eta(P)$, which is obtained as the nonlinear superposition $\eta = e + \alpha^+ \cdot \hat{\epsilon} \cdot \alpha$, of the spontaneous strain $\hat{\epsilon}$ appearing ‘on top of’ the background strain $e(P)$, is the strain measured in the fully deformed state $\mathbf{Y}(P)$, which is the one actually displayed by the system, the system $\mathbf{X}(0)$ again playing the role of the reference system.

In the spirit of Landau’s theory of phase transitions the Landau free energy $F(Q, \epsilon)$ is built from an order parameter part $F_Q(Q)$, an order parameter–strain coupling $F_{Q\epsilon}(Q, \epsilon; \mathbf{X}(P))$ and a purely elastic free energy term $F_\epsilon(\epsilon; \mathbf{X}(P))$ (Toledano and Toledano 1988). The order parameter part $F_Q(Q)$ is usually written as a polynomial in the variables Q which is constructed using the theory of invariants of irreducible representations of the space groups (Kovalev 1993). The construction of the coupling term $F_{Q\epsilon}(Q, \epsilon; \mathbf{X}(P))$ is more tricky. In the present work³ we assume a linear–quadratic coupling of the order parameter to the spontaneous strain, which, as explained above, is measured with respect to the floating background reference system $\mathbf{X}(P)$.

³ The case of bilinear coupling between the order parameter and strain to describe proper ferroelastic HPPTs is treated in Tröster and Schranz (2007).

The corresponding coupling coefficients will be denoted by $d_{ij}^{IJ}(\mathbf{X}(P))$. We thus consider the free energy

$$F(\mathbf{Q}, \hat{\boldsymbol{\epsilon}}; \mathbf{X}(P)) = V(P)\Phi(\mathbf{Q}; \mathbf{X}(P)) + V(P) \sum_{IJij} d_{ij}^{IJ}(\mathbf{X}(P)) Q_I Q_J \hat{\epsilon}_{ij} + F_0(\hat{\boldsymbol{\epsilon}}; \mathbf{X}(P)) \quad (1)$$

where $\Phi(\mathbf{Q}; \mathbf{X}(P))$ denotes the order parameter potential. The pure elastic free energy part $F_0(\hat{\boldsymbol{\epsilon}}; \mathbf{X}(P))$ of the Landau free energy was treated in great detail in (Koppensteiner *et al* 2006).

HPPTs are characterized by the fact that the total strain $\boldsymbol{\eta}$ is not small. However, for phase transitions close to second order there is at least a nonzero pressure interval starting at P_c where the *spontaneous* strain $\hat{\boldsymbol{\epsilon}}$ induced by the nonzero equilibrium order parameter $\bar{\mathbf{Q}}$ can still be treated as infinitesimal. In this approximation the pure elastic free energy part of the Landau potential with respect to $\mathbf{X}(P)$ reads:

$$F_0(\hat{\boldsymbol{\epsilon}}; \mathbf{X}(P)) \approx V(P) \left(-P \sum_i \hat{\epsilon}_{ii} + \frac{1}{2} \sum_{ijkl} C_{ijkl}(\mathbf{X}(P)) \hat{\epsilon}_{ij} \hat{\epsilon}_{kl} \right) \quad (2)$$

where $C_{ijkl}(\mathbf{X}(P))$ are the crystal's thermodynamic elastic constants at pressure P defined by the hydrostatic Cauchy stress tensor $\tau_{ij} = -P\delta_{ij}$. Inserting equation (2) into (1) and minimizing with respect to $\hat{\epsilon}_{ij}$ yields:

$$\sum_{KL} d_{ij}^{KL}(\mathbf{X}(P)) \bar{Q}_K \bar{Q}_L + \sum_{kl} C_{ijkl}(\mathbf{X}(P)) \hat{\epsilon}_{kl}(\bar{\mathbf{Q}}) \equiv 0. \quad (3)$$

Solving equation (3) for $\hat{\epsilon}_{ij}(P)$ and inserting into the equilibrium equation for the order parameter

$$0 \equiv \frac{\partial \Phi(\bar{\mathbf{Q}}; \mathbf{X}(P))}{\partial \bar{Q}_K} + 2 \sum_L d_{ij}^{KL}(\mathbf{X}(P)) \bar{Q}_L \hat{\epsilon}_{ij}(\bar{\mathbf{Q}}) \quad (4)$$

one obtains the renormalized order parameter potential written with respect to the deformed state $\mathbf{X}(P)$:

$$\Phi_R(\mathbf{Q}; \mathbf{X}(P)) := \Phi(\mathbf{Q}; \mathbf{X}(P)) - \frac{1}{2} \sum_{IJKL} Q_I Q_J Q_K Q_L \left(\sum_{ijkl} d_{ij}^{IJ}(\mathbf{X}(P)) C_{ijkl}^{-1}(P) d_{kl}^{KL}(\mathbf{X}(P)) \right). \quad (5)$$

In the spirit of Landau theory we now make the simple but crucial assumption that the Landau and coupling coefficients of the potential depend on P only in a 'geometrical' way, i.e. through volume ratios and geometrical transformation rules between the reference states $\mathbf{X}(P)$ and $\mathbf{X}(0)$, such that the P dependence of the equilibrium order parameter is due to the presence of the order parameter–strain coupling. Transforming equation (5) to the undeformed reference state $\mathbf{X}(0)$, the equilibrium order parameter $\bar{\mathbf{Q}}$ can then be calculated as the minimum of

$$\Phi_R(\mathbf{Q}; \mathbf{X}(0)) = \Phi(\mathbf{Q}; \mathbf{X}(0)) + \sum_{IJij} d_{ij}^{IJ}(\mathbf{X}(0)) e_{ij}(P) Q_I Q_J - \sum_{\substack{IJKL \\ ijkl}} d_{ij}^{IJ}(\mathbf{X}(0)) \frac{T_{ijkl}(P)}{2} d_{kl}^{KL}(\mathbf{X}(0)) Q_I Q_J Q_K Q_L \quad (6)$$

where

$$T_{\text{rost}}(\mathbf{X}(P)) \equiv \frac{V(0)}{V(P)} \sum_{ijkl} \alpha_{ir} \alpha_{jo} C_{ijkl}^{-1}(\mathbf{X}(P)) \alpha_{ks} \alpha_{lt} \quad (7a)$$

$$d_{mn}^{IJ}(\mathbf{X}(P)) \equiv \frac{V(0)}{V(P)} \sum_{ij} \alpha_{mi} d_{ij}^{IJ}(\mathbf{X}(0)) \alpha_{nj} \quad (7b)$$

and the total (Lagrange) strain η_{ij} turns out to be

$$\eta_{ij} = e_{ij} - \sum_{KL} \bar{Q}_K \bar{Q}_L \sum_{kl} d_{kl}^{KL}(\mathbf{X}(0)) T_{ijkl}(P). \quad (8)$$

Applying the above procedure and employing the usual assumptions concerning the temperature behaviour of the Landau parameters, one is able to calculate the pressure and temperature dependences of thermodynamic quantities like specific heat, strains and elastic constants, soft mode behaviour, etc near HPPTs. A concrete example of the above theory at work will be given below. However, the above constructions obviously rely on knowledge of the pressure dependence of the elastic constants $C_{ijkl}(\mathbf{X}(P)) \equiv C_{ijkl}(P)$ (or equivalently, the Birch coefficients $B_{ijkl}(P) = P(\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}) + C_{ijkl}(P)$) and the resulting background strains $e_{ij}(P)$. Note that these quantities also appear in the renormalized free energy density equation (6). To calculate it we proceed in the following way.

For crystal classes that develop no shear strains under hydrostatic pressure (cubic, tetragonal, hexagonal, orthorhombic) the deformation tensor $\alpha_{ij}(P) = \alpha_i(P)\delta_{ij}$ is diagonal and the axial compressibilities satisfy the equations

$$-\frac{1}{\alpha_i(P)} \frac{d\alpha_i(P)}{dP} = \sum_k S_{ik}(P) =: \kappa_i(P) \quad (i = 1, 2, 3) \quad (9)$$

with the initial conditions $\alpha_i(0) = 1$, where $S_{ij}(P) := B_{ij}^{-1}(P)$ denote the compliance tensor elements and we switched to Voigt notation. Therefore the deformation tensor components $\alpha_i(P)$ as well as the finite strain tensor components $\epsilon_{ij}(P)$ or lattice parameters $a_i(P)$ can be easily calculated by integrating equation (9), once the functions $S_{ik}(P)$, $i, k = 1, 2, 3$ are known.

In our recent work (Tröster *et al* 2002) we proposed the expansion

$$S_{ij}(P) = \frac{\kappa(P)}{\kappa_0} \left(S_{ij}^0 + \sum_{n=1}^{\infty} \kappa_{ij}^n P^n \right) \quad (10)$$

where $\kappa(P)$ is the bulk compressibility, $\kappa_0 = \kappa(P = 0)$ and S_{ij}^0 denotes the zero-pressure compliance. The expansion coefficients κ_{ij}^n obey the sum rule $\sum_{ij} \kappa_{ij}^n = 0 \forall n \in \mathbb{N}$. Equation (10), which is exact at infinite n , yields an elegant parametrization of the pressure dependence of the compliance tensor, since it essentially factorizes out the main nonlinearity of the compliance through the bulk compressibility $\kappa(P)$. The elastic anisotropy is taken into account by expanding the remainder in powers of P , as we anticipate that the very nature of the expansion allows it to be truncated at low orders with good accuracy. Indeed we have shown in a very recent work (Koppensteiner *et al* 2006) that even a low order truncation of our ansatz equation (10) excellently fits the experimental high pressure data of olivine, fluorite, garnet, magnesium oxide and stishovite. In fact, for all these examples a truncation at order $n = 1$ turned out to be sufficient to produce accurate results, the only exception being magnesium oxide, where the expansion equation (10) had to be taken to $n = 2$. This very encouraging result implies that our new thermodynamic theory indeed allows for a dramatic reduction of the number of fit parameters as compared to conventional nonlinear approaches. Table 1 shows the number of relevant (nonshear) elastic constants of second, third and fourth order for various point group symmetries. Our approach requires only $q_2 - 1$ additional unknown parameters κ_{ij}^1 (at order $n = 1$), whereas a fit of an expansion of the elastic energy including nonlinear elastic constants up to fourth order introduces $q_3 + q_4$ additional fit parameters. For example, in the case of cubic I symmetry, our new approach requires $q_2 - 1 = 1$ fit parameters as compared to the $q_2 + q_3 = 7$ unknown parameters of a conventional fourth order nonlinear theory. For lower symmetry the advantages of our approach are even more obvious. For instance, in the

Table 1. Number q_2, q_3, q_4 of nonshear elastic constants of second, third and fourth order (Roy and Dasgupta 1988, Brendel 1979).

	Cubic I (432, $\bar{4}3m$ $m\bar{3}m$)	Cubic II (23, $m\bar{3}$)	Hexagonal I (622, $6mm$ $\bar{6}m2, 6/mmm$)	Hexagonal II (6, $\bar{6}6/m$)	Tetragonal I (422, $4mm$ $\bar{4}2m, 4/mmm$)	Tetragonal II (4, $\bar{4}$ $4/m$)	Orthorhombic (222, $mm2$ mmm)
q_2	2	2	4	4	4	4	6
q_3	3	4	6	6	6	7	10
q_4	4	5	13	13	9	9	15

case of orthorhombic symmetry our new parametrization needs five parameters, which should be compared to a total of 25 unknowns for conventional nonlinear elasticity!

The combination of high pressure Landau theory and the use of the expansion (10) for the background system $\mathbf{X}(P)$ is illustrated by an analysis of measurements of tetragonal BaCr(Si₄O₁₀) single crystals. Using x-ray diffraction, the P dependence of lattice parameters $a_1(P) = a_2(P)$, $a_3(P)$, and the unit cell volumes $V(P)$ were measured in great detail at room temperature in a diamond anvil cell (Tröster *et al* 2002).

One finds a tetragonal–tetragonal HPPT at approximately 2.24 GPa, characterized by a discontinuity in $a_1(P)$, $a_3(P)$ and $V(P)$. Consistent with the observed pressure hysteresis behaviour, the transition can be classified as being (weakly) of first order. The order parameter part is constructed in the following standard way (Kovalev 1993): the symmetry reduction $P4/ncc$ to $P4_212$ is driven by the one-dimensional irreducible representation τ_2 at the wavevector $\mathbf{k} = \mathbf{0}$, yielding a one-component order parameter Q , which is zero in the paraphase ($P < P_c$) and nonzero in the distorted phase ($P > P_c$). For $\Phi(Q, \mathbf{X})$ we assume

$$\Phi(Q, \mathbf{X}) = \frac{A}{2}Q^2 + \frac{B}{4}Q^4 + \frac{C}{6}Q^6 \quad (11)$$

where $A, C > 0$. The tetragonal symmetry also dictates $d_1(\mathbf{X}) = d_2(\mathbf{X}) \neq d_3(\mathbf{X})$.

Let $K_0 := \kappa^{-1}(0)$ denote the isothermal bulk modulus at $P = 0$. The Murnaghan equation of state (MEOS) (Anderson 1995)

$$v(P) := \frac{V(P)}{V(0)} = \left(1 + K'_0 P/K_0\right)^{-1/K'_0} \quad (12)$$

which is based on the simple ansatz $\kappa^{-1}(P) =: K(P) = K_0 + K'_0 P$, is frequently used to describe (P, V) data and is known to usually reproduce the values of $K(P)$ correctly up to volume changes somewhat larger than $v(P) > 0.9$ while being algebraically much simpler than other approaches such as the ‘Vinet’ or the ‘Birch–Murnaghan’ EOS (Anderson 1995, Angel 2000b) used for higher compression ranges. Figure 2 shows corresponding fits of unit cell volume and axes of BaCr(Si₄O₁₀) using the parameter values of table 2. Note, however, that our theory can in principle be used in combination with any of these EOS, or even a function $V(P)$ derived from an experimental measurement or a computer simulation. With these values our model confines possible pressure ranges for hysteresis effects to 2.2–2.4 GPa. One also calculates that the geometrical error introduced in assuming the spontaneous strain $\hat{\epsilon}$ to be infinitesimal is smaller than 0.9%, yielding an error $< 0.1\%$ in the total strain η .

Figure 3 shows the pressure dependence of the bulk modulus of BaCr(Si₄O₁₀) calculated from the experimental data of $V(P)$ compared to the predictions of the different approaches discussed above. It is clearly evident that the conventional fitting procedure, which is based on a piecewise fitting of EOS in the high and low pressure phase, respectively, underestimates the elastic anomaly by at least a factor of two, whereas the present high pressure adapted Landau theory reproduces the elastic anomaly very well. The same behaviour is found for the axial

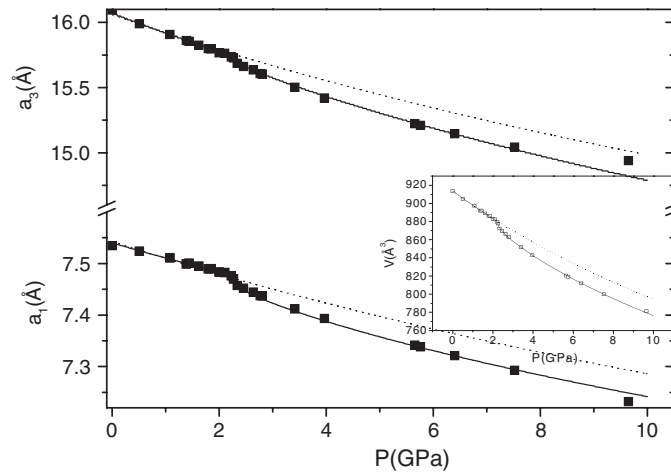


Figure 2. Pressure dependence of lattice parameters and unit cell volume of BaCr(Si₄O₁₀). Points are measured data, lines are fits using the present theory.

Table 2. Fit parameters for the high pressure Landau theory of BaCr(Si₄O₁₀).

BaCr(Si ₄ O ₁₀)	
A	0.45 GPa
B	-0.2 GPa
C	20 GPa
$a_1(0) = a_2(0)$	7.535 Å
$a_3(0)$	16.09 Å
κ_1^0	0.0035 GPa ⁻¹
κ_3^0	0.001 GPa ⁻¹
S_{11}^0	0.0035 GPa ⁻¹
S_3^0	0.0089 GPa ⁻¹
K'_0	4.1
κ_{11}^1	1.9×10^{-4} GPa ⁻²
κ_{12}^1	-1.7×10^{-4} GPa ⁻²
κ_{13}^1	2.3×10^{-4} GPa ⁻²
d_1	13.75 GPa ⁻¹
d_3	-0.33 GPa ⁻¹

incompressibilities (figure 4). It is worth noting that a very similar softening was also observed in other examples of pressure-induced phase transitions, notably for the bulk modulus of solid C₆₀ near its fcc–sc transition (Pintschovius *et al* 1999) and for the longitudinal acoustic modes near the cubic–tetragonal transition of BaTiO₃ (Ishidate and Sasaki 1989).

3. Summary

Summarizing, our theory allows to compute a wealth of experimental observables (e.g. lattice parameters, elastic constants, specific heat, soft modes, etc) from a quite transparent

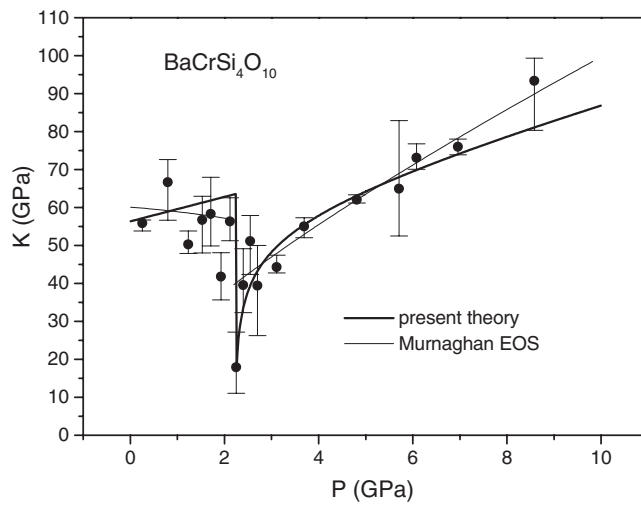


Figure 3. Pressure dependence of the bulk modulus $K(P)$ calculated from the experimental data of $V(P)$ (points). The lines show calculations based on piecewise EOS fitting (thin line) and the present high pressure Landau theory (thick line).

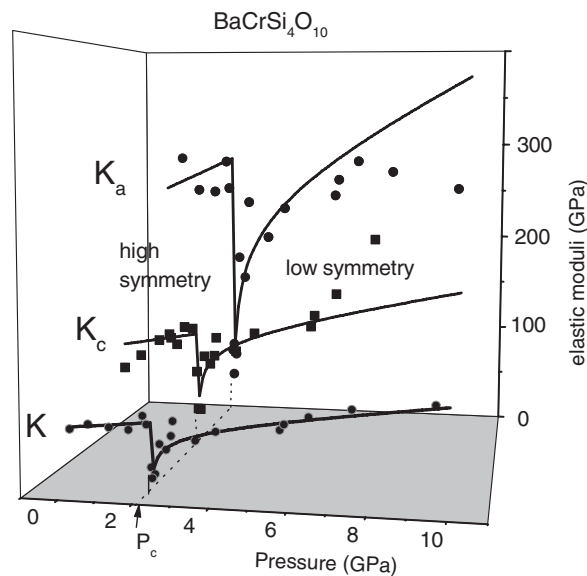


Figure 4. Pressure dependence of axial incompressibilities K_a , K_c calculated from the lattice parameters a_1 , a_3 (points) and the bulk modulus K compared with the results of the present Landau theory (lines).

thermodynamic model based on coupling finite strain elasticity to Landau theory. There are several advantages of this new approach to HPPTs. First there is a drastic reduction of fit parameters as compared to an expansion in terms of nonlinear elastic constants (table 1). Moreover the present approach allows for a direct connection to EOS fitting procedures. Compared to the method of piecewise EOS fitting the main advantage of our method is that

it allows for a unified consistent description of high and low symmetry phases with a single set of parameters.

Of course there are a few assumptions made in the derivation of our theory, which may impose some limitations on its applicability to real cases. These assumptions are summarized as follows:

- The Landau theory is currently derived for HPPTs of the group–subgroup type, so-called ‘Landau-type’ phase transitions. However, we plan to extend our theory to also include the important class of *reconstructive phase transitions* following the theoretical approach of Toledano and Dmitriev (1996).
- The spontaneous strain $\hat{\epsilon}_{ij}$ occurring at the HPPT is assumed to be infinitesimal. This assumption is obviously justified for a second or close-to-second order transition in the vicinity of the critical pressure but has to be checked against experimental data for any given material in other cases. However, we emphasize that the ‘background’ strains $e_{ij}(P)$ as well as the total strains $\eta_{ij}(P)$ are treated as fully finite strains, since these are usually large at HPPTs.
- For the derivation of the pure elastic part of the free energy, as well as for the calculation of the ‘background’ strains, the longitudinal part of the compliance tensor (inverse Birch coefficients) is expanded as a function of pressure in a very efficient way (see equation (10)). In Koppensteiner *et al* (2006) we have shown that this parametrization works very well up to very high pressures for olivine, fluorite, garnet, magnesium oxide and stishovite, i.e. the P expansion can be truncated at very low order without loss of precision. Nevertheless, for any given material under investigation it has to be checked at which order the P expansion can be truncated.
- In applying the present theory to a concrete HPPT, the order parameter part of the Landau potential is—as always in Landau theory—expanded into a polynomial in the order parameter components, whose coefficients together with the coupling coefficients (or order parameter–strain coupling) are treated as fit parameters. Our approach relies on the assumption of pressure independence of the ‘pure’ Landau potential and coupling coefficients, up to the volume changes captured in the overall factor $V(P)/V(0)$. This is an obvious thing to do, and is justified in the spirit of temperature-driven Landau theory (Tröster *et al* 2005), namely that it does represent a good approximation near the critical pressure P_c . In a broader pressure range away from P_c the Landau-coefficients may nevertheless become slightly pressure dependent. However, any such ‘nontrivial’ pressure dependence actually signals additional nonzero couplings between the order parameter and strain *beyond* the linear–quadratic term considered, a fact which is also well-known from the infinitesimal version of the theory.
- Our theory is capable of dealing with ‘Landau-type’ high pressure phase transitions between arbitrary group–subgroup related symmetries. However, in applications to experimental situations, at present our parametrization of the pressure dependence of the compliance tensor of the background system, which is needed to define the ‘base lines’ for determining the spontaneous strains, works only for longitudinal components. It is only due to this limitation that applications of the theory are at present practically restricted to HPPTs involving cubic, tetragonal, orthorhombic or hexagonal structures, i.e. crystal classes where no shear components of strain are induced by hydrostatic pressure. However, it is possible to treat more general cases as soon as the pressure dependence of the shear components of the compliance tensor is known in addition to the longitudinal ones. Further work in this direction is in progress.

Acknowledgments

Support by the Austrian FWF (P19284-N20) and the *University of Vienna* (Initiativkolleg IK 1022-N, and research focus *Materials Science 'Bulk Nanostructured Materials'*) is gratefully acknowledged.

References

- Anderson O L 1995 *Equations of State of Solids for Geophysics and Ceramic Sciences* (Oxford: Oxford University Press)
- Angel R J 2000a High-pressure structural phase transitions in *Transformation Processes in Minerals (Reviews in Mineralogy and Geochemistry* vol 39) ed S A T Redfern and M A Carpenter (Chantilly, VA: USA) p 85
- Angel R J 2000b Equations of state in *High-Temperature-High-Pressure Crystal Chemistry (Reviews in Mineralogy* vol 40) ed R M Hazen (Chantilly, VA: USA) pp 35–60
- Bergman D J and Halperin B I 1976 *Phys. Rev. B* **13** 2145–75
- Bratkovsky A M, Salje E K H, Marais S C and Heine V 1995 *Phase Transit.* **55** 79–126
- Brendel R 1979 Crystal classes *Acta Crystallogr. A* **35** 523–33
- Carpenter M A, Salje E K H and Graeme-Barber A 1998 *Eur. J. Mineral.* **10** 621–91
- Chesnut G N and Vohra Y K 2000 *Phys. Rev. B* **62** 2965–8
- Dove M T 1997 *Am. Mineral.* **82** 213–44
- Giddy A P, Dove M T and Heine V 1989 *J. Phys.: Condens. Matter* **1** 8327–35
- Ishidate T and Sasaki S 1989 *Phys. Rev. Lett.* **62** 67–70
- Koppensteiner J, Tröster A and Schranz W 2006 *Phys. Rev. B* **74** 014111
- Kovalev O V 1993 *Representation of the Crystallographic Space Groups* ed H T Stokes and D M Hatch (New York: Gordon and Breach)
- Krüger T and Holzzapfel W B 1992 *Phys. Rev. Lett.* **69** 305–7
- Meyer H W, Carpenter M A, Graeme-Barber A, Sondergeld P and Schranz W 2000 *Eur. J. Mineral.* **12** 1139
- Parlinski K, Schranz W and Kabelka H 1989 *Phys. Rev. B* **39** 488
- Pérez-Mato J M, Ivantchev S, Garca A and Etxebarria I 2000 *Ferroelectrics* **236** 93–103
- Pintsohiovius L, Blaschko O, Krexner G and Pyka N 1999 *Phys. Rev. B* **59** 11020–6
- Roy D and Dasgupta 1988 *Lattice Theory of Elastic Constants* ed S Senegupta (Switzerland: Transtech)
- Rubtsov A N, Hlinka J and Janssen T 2000 *Phys. Rev. E* **61** 126–31
- Salje E K H 1990 *Phase Transitions in Ferroelastic and Coelastic Crystals* (Cambridge: Cambridge University Press) pp 1–229
- Salje E K H, Wruck B and Thomas H 1991 *Z. Phys. B* **82** 399
- Salje E K H 1992 *Phys. Rep.* **215** 49–99
- Schulte O and Holzzapfel W B 1995 *Phys. Rev. B* **52** 12636–9
- Sondergeld P, Schranz W, Tröster A, Carpenter M A, Libowitzky E and Kityk A V 2000 *Phys. Rev. B* **62** 6143
- Toledano J C and Toledano P 1988 *The Landau Theory of Phase Transitions* (Singapore: World Scientific)
- Toledano P and Dmitriev V 1996 *Reconstructive Phase Transitions in Crystals and Quasicrystals* (Singapore: World Scientific)
- Tröster A, Dellago C and Schranz W 2005 *Phys. Rev. B* **72** 094103
- Tröster A and Schranz W 2007 *Ferroelectrics* invited paper in honor of V. Ginzburg's 90th birthday to appear
- Tröster A, Schranz W and Miletich R 2002 *Phys. Rev. Lett.* **88** 055503