2.06 Theory and Practice – Thermodynamics, Equations of State, Elasticity, and Phase Transitions of Minerals at High Pressures and Temperatures

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2.06.1 Thermodynamics of Crystals

Thermodynamics provides the general basis for the theory of structure and properties of matter. This chapter presents only as much thermodynamics as needed for good comprehension of geophysics, and at a relatively advanced level. For further reading the reader is referred to Landau and Lifshitz (1980), Chandler (1987), Wallace (1998), and Bowley and Sánchez (1999).

2.06.1.1 Thermodynamic Potentials

If one considers some system (e.g., a crystal structure) at temperature $T = 0$ K and pressure $P = 0$, the equilibrium state of that system corresponds to the minimum of the internal energy $E$:

$$ E \rightarrow \text{min} \quad [1] $$

that is, any changes (e.g., atomic displacements) would result in an increase of energy. The internal energy itself is a sum of the potential and kinetic energies of all the particles (nuclei, electrons) in the system.

The principle [1] is valid in only two situations: (1) at $T = 0$ K, $P = 0$, and (2) at constant $V$ (volume) and $S$ (entropy), that is, if we impose constraints of constant $S, V$, the system will adopt the lowest-energy state. Principle [1] is a special case of a more general principle that the thermodynamic potential $W$ describing the system be minimum at equilibrium:

$$ W \rightarrow \text{min} \quad [2] $$

As already mentioned, at constant $V, S$, $W_{V, S} = E \rightarrow \text{min}$.

At constant $P, S$, the appropriate thermodynamic potential is the enthalpy $H$:

$$ W_{P, S} = H = E + PV \rightarrow \text{min} \quad [3] $$

At constant $V, T$, the Helmholtz free energy $F$ is the thermodynamic potential:

$$ W_{V, T} = F = E - TS \rightarrow \text{min} \quad [4] $$

At constant $P, T$ (the most frequent practical situation), the relevant thermodynamic potential is the Gibbs free energy $G$:

$$ W_{P, T} = G = E + PV - TS \rightarrow \text{min} \quad [5] $$

The minimum condition implies that

$$ \frac{\partial W}{\partial x_i} = 0 \quad [6] $$

However, this condition is also satisfied for maxima of the thermodynamic potential, and for saddle points (Figure 1). To exclude saddle points and maxima, one has to make sure that the matrix of second derivatives of $W$ with respect to all the degrees of freedom (in case of a crystal structure, with respect to atomic coordinates and lattice parameters):

$$ H_{ij} = \frac{\partial^2 W}{\partial x_i \partial x_j} \quad [7] $$

be positive definite:

$$ \det H_{ij} > 0 \quad [8] $$

Still, there may be a large (or infinite) number of minima. The equilibrium state corresponds to the lowest minimum of $W$ (the global minimum), whereas all the other minima are called local and correspond to metastable states. Local minima have the property of stability to an infinitesimal displacement (after any such displacement the system returns to the initial state), but one can always find a sufficiently large energy fluctuation that will irreversibly destroy the metastable state.

2.06.1.2 Differential Relations

From the first law of thermodynamics one has

$$ dE = -P \, dV + T \, dS \quad [9] $$

Applying Legendre transformations, the following relations can be obtained:

$$ dH = V \, dP + T \, dS \quad [10] $$

$$ dF = -P \, dV - S \, dT \quad [11] $$

$$ dG = V \, dP - S \, dT \quad [12] $$

When there is thermodynamic equilibrium between two phases (denoted 1 and 2) at given $P$ and $T$,
Moving along the two-phase equilibrium line in $P$–$T$ space requires $dG_1 = dG_2$, that is,

$$
\Delta V \, dP - \Delta S \, dT = 0
$$

or, in a different form,

$$
\frac{dP}{dT} = \Delta S \Delta V
$$

This is the famous Clausius–Clapeyron equation.

Using eqns [9]–[12], one can express various thermodynamic parameters:

$$
P = - \left( \frac{\partial E}{\partial V} \right)_S = - \left( \frac{\partial F}{\partial V} \right)_T
$$

$$
V = \left( \frac{\partial H}{\partial P} \right)_S = \left( \frac{\partial G}{\partial P} \right)_T
$$

$$
T = \left( \frac{\partial E}{\partial S} \right)_V = \left( \frac{\partial H}{\partial S} \right)_P
$$

$$
S = - \left( \frac{\partial F}{\partial V} \right)_S = - \left( \frac{\partial G}{\partial T} \right)_P
$$

Using the Maxwell relations, a number of important thermodynamic relations are derived, for example,

$$
\frac{\partial S}{\partial P} = \frac{\alpha}{\kappa T}
$$

$$
\frac{\partial S}{\partial V} = \frac{C_P}{\alpha V T}
$$

$$
\frac{\partial S}{\partial P} = - \alpha V
$$

$$
\frac{\partial T}{\partial P} = \frac{\alpha V T}{C_P}
$$

$$
\frac{\partial V}{\partial T} = - \frac{C_P}{\alpha S T}
$$

$$
\frac{\partial P}{\partial T} = \alpha k T
$$

In eqns [23]–[28] we used thermal expansion

$$
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P
$$

isothermal bulk modulus

$$
K_T = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S
$$

and isobaric heat capacity

$$
C_P = \left( \frac{\partial E}{\partial T} \right)_P
$$

We note, on passing, that the bulk modulus and the heat capacity depend on the conditions of measurement. There are general thermodynamic equations relating the heat capacity at constant pressure (isobaric) and constant volume (isochoric):

$$
C_P = C_V \left( 1 + \frac{\alpha^2 k T V}{C_V} \right)
$$

and bulk modulus at constant temperature (isothermal) and at constant entropy (adiabatic):

$$
K_S = K_T \left( 1 + \frac{\alpha^2 k T V}{C_P} \right)
$$

The most interesting of eqns [23]–[28] are eqn [26], describing the increase of the temperature of a body on adiabatic compression (e.g., in shock waves, and also inside rapidly convecting parts of planets), and eqn [28], describing thermal pressure. These equations are important for thermal equations of state and for calculating the temperature distributions inside planets.

### 2.06.1.3 Partition Function

Let us consider a system with energy levels $E_i$ corresponding to the ground state and all the excited states. The probability to find the system in the $i$th state is proportional to $e^{-\beta E_i}$, where $\beta = 1/(k_B T)$ ($k_B$ is the Boltzmann constant).

More rigorously, this probability $p_i$ is given as

$$
p_i = e^{-\beta E_i} \sum_i e^{-\beta E_i}
$$

The denominator of this equation is called the partition function $Z$:

$$
Z = \sum_i e^{-\beta E_i}
$$

where the summation is carried out over all discrete energy levels of the system. The partition function is
much more than a mere normalization factor; it plays a fundamental role in statistical physics, providing a link between the microscopic energetics and the macroscopic thermodynamics. Once \( Z \) is known, all thermodynamic properties can be obtained straightforwardly (e.g., Landau and Lifshitz, 1980). For instance, the internal energy

\[
E = \sum \beta_i E_i = \sum \frac{E_i e^{-\beta E_i}}{z} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_V
\]

From this one can derive a very important expression for the Helmholtz free energy

\[
F = -\frac{1}{\beta} \ln Z = -k_B T \ln Z
\]

and the heat capacity at constant volume (From eqn [39] one can derive (see Dove, 2003) the following important formula: \( C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \):)

\[
C_V = -\frac{k_B \beta^2}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)_V + \frac{k_B \beta^2}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} \right)_V
\]  

Unfortunately, in many real-life cases it is practically impossible to obtain all the energy levels – neither experimentally nor theoretically, and therefore the partition function cannot be calculated exactly. However, for some simplified models it is possible to find the energy levels and estimate the partition function, which can then be used to calculate thermodynamic properties.

Below we consider the harmonic approximation, which plays a key role in the theory of thermodynamic properties of crystals. It gives a first approximation to the distribution of the energy levels \( E_n \) which is usually accurate for the most-populated lowest excited vibrational levels. The effects not accounted for by this simplified picture can often be included as additive corrections to the harmonic results.

2.06.1.4 Harmonic Approximation

The harmonic oscillator is a simple model system where the potential energy \( (U) \) is a quadratic function of the displacement \( x \) from equilibrium, for example, for a simple diatomic molecule

\[
U(x) = U_0 + \frac{1}{2} k x^2
\]

where \( U_0 \) is the reference energy and \( k \) is the force constant.

The energy levels of the harmonic oscillator can be found by solving the Schrödinger equation with the harmonic potential [40]; the result is an infinite set of equi-spaced energy levels:

\[
E_n = \left( \frac{n}{2} + \frac{1}{2} \right) \hbar \omega
\]

where \( \hbar \) is Planck’s constant, \( \omega \) is the vibrational frequency of the oscillator, and integer \( n \) is the quantum number; \( i = 0 \) for the ground state, and \( i \geq 1 \) for excited states. Energy levels in a true vibrational system are well described by [41] only for the lowest quantum numbers \( n \), but these represent the most populated, and thus the most important vibrational excitations.

A very interesting feature of [41] is that even when \( i = 0 \), that is, when there are no vibrational excitations (at 0 K), there is still a vibrational energy equal to \( \hbar \omega/2 \). This energy is called zero-point energy and arises from quantum fluctuations related to the Heisenberg uncertainty principle.

With [41] the partition function for the harmonic oscillator is rather simple:

\[
Z = \frac{1}{1 - e^{-\hbar \omega/k_B T}}
\]

This allows one to calculate thermodynamic functions of a single harmonic oscillator (as was first done by Einstein):

\[
E_{\text{vib}}(\omega, T) = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{ \exp(\hbar \omega/k_B T) - 1}
\]

\[
C_V,\text{vib}(\omega, T) = k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp(\hbar \omega/k_B T)}{ (\exp(\hbar \omega/k_B T) - 1)^2}
\]

\[
S_{\text{vib}}(\omega, T) = -k_B \ln[1 - \exp(-\hbar \omega/k_B T)] + \frac{\hbar \omega}{T \exp(\hbar \omega/k_B T) - 1}
\]

\[
F_{\text{vib}}(\omega, T) = \frac{1}{2} \hbar \omega + k_B T \ln \left[ 1 - \exp \left( \frac{-\hbar \omega}{k_B T} \right) \right]
\]

The first term in [43] is the zero-point energy originating from quantum motion of atoms discussed above. The second, temperature-dependent term gives the thermal energy according to the Bose–Einstein distribution. The thermal energy (or heat
acoustic modes the phonon spectrum can be described, to a first approximation, by a parabolic function:

\[
g(\omega) = 9N \left( \frac{\hbar}{k_B \theta_D} \right)^3 \omega^2 \tag{51}
\]

truncated at the maximum frequency \( \omega_D = (k_B \theta_D)/\hbar \), where \( \theta_D \) is the Debye temperature.

With this \( g(\omega) \) the thermodynamic functions take the following form:

\[
E_{\text{vib}} = \frac{9}{8} k_B N \theta_D + 3 k_B N T D \left( \frac{\theta_D}{T} \right) \tag{52}
\]

\[
C_V(T) = \left( \frac{dE_{\text{vib}}}{dT} \right)_V = 3 k_B N \left[ 4 D \left( \frac{\theta_D}{T} \right) - \frac{3}{2} \left( \frac{\theta_D}{T} \right)^2 \right] \tag{53}
\]

\[
S(T) = \int_0^T \frac{C_V}{T} dT = k_B N \left[ 4 D \left( \frac{\theta_D}{T} \right) - 3 \ln(1 - e^{\theta_D/T}) \right] \tag{54}
\]

where

\[
D(x) = \frac{3}{x^3} \int_0^x \frac{d\lambda}{e^\lambda - 1}, \quad x = \frac{\theta_D}{T} \tag{55}
\]

The first term in [52] is the zero-point energy in the Debye model, the second term is the heat content. The Debye temperature is determined by the elastic properties of the solid or, more precisely, its average sound velocity \( \langle v \rangle \):

\[
\theta_D = \frac{\hbar}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{1/3} \langle v \rangle \tag{55}
\]

The mean sound velocity can be accurately calculated from the elastic constants tensor (Robie and Edwards, 1966). Usually, however, an approximate formula is used:

\[
\langle v \rangle = \left( \frac{1}{v_p} + \frac{2}{v_S} \right)^{-1/3} \quad \text{[56]}
\]

where \( v_p \) and \( v_S \) are the longitudinal and transverse sound velocities, respectively. Later in this chapter we shall see as to how to calculate these velocities. The advantages of the Debye model are its relative simplicity and correct low- and high-temperature limits for all thermodynamic properties. The crucial disadvantage is that it is hardly capable of giving accurate entropies for anything other than monatomic lattices. Deep theoretical analyses of this model and its critique can be found in Seitz (1949) and Kieffer (1979). In Figure 2 we compare the phonon spectra and \( C_V \) obtained in the Debye model and in full-phonon harmonic calculations done with the same model.

2.06.1.4.1 Debye model

In early works, the phonon density of states \( g(\omega) \) had often been simplified using the Debye model. For the
interatomic potential (see Oganov et al. (2000)). The phonon spectra are very different, but heat capacities are reasonably close (only below ~500 K, the disagreement is appreciable).

2.06.1.4.2 General harmonic potential

Let us now come back to the general harmonic case. First of all, the potential [40] describing a simple elastic spring or a diatomic molecule can be generalized to the case of three-dimensional structures. One can expand the crystal potential energy $U$ around the equilibrium configuration in terms of displacements $u_i^j(l)$ of $i$th atoms in the $l$th unit cell along each $a$th coordinate (Cartesian axis):

$$U = U_0 + \sum_{i,l,a} \Phi_i^a(l) u_i^a(l) + \frac{1}{2!} \sum_{i < l', i', j, j', a, b} \Phi_{a \beta}^{i j}(l') u_i^a(l) u_j^b(l') + \frac{1}{3!} \sum_{i < l', j < l''} \Phi_{a \beta \gamma}^{i j}(l''') u_i^a(l) u_j^b(l') u_k^c(l'') + \cdots$$

[57]

where

$$\Phi_i^a(l) = \frac{\partial U}{\partial u_i^a(l)}$$

$$\Phi_{a \beta}^{i j}(l') = \frac{\partial^2 U}{\partial u_i^a(l') \partial u_j^b(l')}$$

[58]

$$\Phi_{a \beta \gamma}^{i j}(l''') = \frac{\partial^3 U}{\partial u_i^a(l') \partial u_j^b(l') \partial u_k^c(l'')}$$

At equilibrium $\Phi_i^a(l) = 0$, so neglecting third- and higher-order terms (called anharmonic terms), we obtain the harmonic expansion of the potential energy:

$$U = U_0 + \frac{1}{2} \sum_{i < l', i', j, j', a, b} \Phi_{a \beta}^{i j}(l') u_i^a(l) u_j^b(l')$$

[59]

The generalized harmonic potential [59] includes noncentral forces, due to which directions of the displacement and force may differ. In spite of the complicated mathematical form of [59], it is really analogous to [40]. It also corresponds to a set of phonons, which are again noninteracting and have the same quantization as given by [41]. For each vibrational mode, the partition function is expressed as [42], and thermodynamic properties are described by [47]–[50].

The use of the harmonic approximation, neglecting third- and higher-order terms in the interatomic potential, leads to a number of fundamental errors. The phonon frequencies in this approximation do not depend on temperature or volume, and are noninteracting. This leads to a simple interpretation of experimentally observed vibrational spectra and greatly simplifies the calculation of thermodynamic properties [47]–[50], but noninteracting phonons can freely travel within the crystal, leading to an infinite thermal conductivity of the harmonic crystal. In a real crystal, thermal conductivity is, of course, finite due to phonon–phonon collisions, scattering on defects, and finite crystal size. In the harmonic approximation, the energy needed to remove an atom from the crystal is infinite – therefore,
diffusion and melting cannot be explained within this approximation. The same can be said about displacive phase transitions – even though the harmonic approximation can indicate such a transition by showing imaginary phonon frequencies, calculation of properties of the high-temperature dynamically disordered phase is out of reach of the harmonic approximation. In the harmonic approximation there is no thermal expansion, which obviously contradicts experiment. Related to this is the equality $C_V = C_P$, whereas experiment indicates $C_V < C_P$ (see [32]). In a harmonic crystal, at high temperatures $C_V$ tends exactly to the Dulong–Petit limit of $3Nk_B$, whereas for anharmonic crystals this is not the case (see Section 2.06.1.8 for more details on anharmonicity).

The first approximation correcting many of these drawbacks, the quasiharmonic approximation, as well as methods to account for higher-order anharmonicity will be discussed later in this chapter, but now let us explore some more fundamental aspects of thermodynamics.

### 2.06.1.5 Quantum Effects in Thermodynamics

Quantum effects are of fundamental importance for thermodynamic properties. Insufficiency of classical mechanics is apparent in any experimental determinations of the heat capacity at low temperatures.

According to classical mechanics, every structural degree of freedom has $(k_BT)/2$ worth of kinetic energy. In a harmonic solid, there is an equal amount of potential energy, so the total vibrational energy equals $3Nk_BT$; and the heat capacity $C_V$ is then $3N$. In a stark contrast, experiment shows $C_V$ going to zero as $T^{-3}$ at low temperatures. Similarly, thermal expansion goes to zero at low temperatures – in contrast to classical theory, predicting a finite value. A very important consequence is for the entropy: if, as the classical approximation claims, $C_V = 3Nk_B$ at all temperatures, then the entropy $(S = \int_0^\infty (C_V/T)\,dT)$ is infinite.

The partition function [35] includes the relevant quantum effects, and do harmonic expression [43]–[50] for thermodynamic functions. In the classical approximation, the partition function is

$$Z_{\text{class}} = \frac{1}{N!\lambda^{3N}} \int \int e^{-\frac{U(r)}{k_B} + F_{\text{class}}(\rho)} \, dr \, d\rho \quad [60]$$

The denominator in this definition already accounts for some quantum effects. There, one has $N!$ to account for indistinguishability of same-type particles, and $\lambda^{3N}$ that takes into account the fact that quantum states are discrete and very small differences in coordinates/momenta of particles may correspond to the same quantum state. Nevertheless, this definition is classical – since it involves integration in the phase space, rather than summation over discrete quantum states and since some essentially quantum effects (such as exchange) are not present in [60].

According to the uncertainty principle, quantum particles are never at rest and there is quantum motion of atoms even at 0 K (zero-point motion). The corresponding energy, arising from quantum motion in a potential field, is called the zero-point energy, which we already encountered in harmonic expressions [43], [46], [47], and [50]. The magnitude of zero-point motion is significant – it can contribute more than 50% of the total experimentally observed atomic mean-square displacements at room temperature.

It is important that at temperatures significantly exceeding the characteristic temperatures $\theta$ of all the vibrational modes ($\theta = (\hbar c/k_B)$), classical expressions will be correct. This circumstance justifies the application of methods based on classical mechanics (molecular dynamics, Monte Carlo, etc.) in simulations of materials at high temperatures. At low temperatures, where quantum effects dominate, one could use the harmonic approximation (or, better, the quasiharmonic approximation – see below) or include quantum corrections to classical results.

The classical free energy can be calculated as

$$F_{\text{class}} = E_0 - k_B T \ln Z_{\text{class}} \quad [61]$$

where $E_0$ is the internal energy of a static crystal structure. The quantum correction to [61] per atom in the lowest order is (Landau and Lifshitz, 1980)

$$\Delta F = F - F_{\text{class}} = \frac{\hbar^2}{24k_B T^2} \left\langle \sum_i \frac{(\nabla_i^2 U)^2}{m_i} \right\rangle$$

$$= \frac{\hbar^2}{24k_B T} \left\langle \sum_i \nabla_i^2 U \right\rangle \quad [62]$$

where is $\nabla_i^2$ is the Laplacian with respect to the coordinates of the $i$th atom. Higher-order ($\hbar^3$ and higher) corrections are needed only at temperatures below $\sim (\theta_D/2)$. Quantum corrections to other properties can be worked out by differentiating [62] (see Matsui (1989) and Figure 3).
Other possibilities to incorporate quantum corrections into classical results can be done using (1) path integral formalism (see Allen and Tildesley, 1987), (2) phonon density of states $g(\omega)$, which can be calculated classically, and quasiharmonic formulas. Montroll (1942, 1943) has formulated a method of calculating thermodynamic properties of a solid without the knowledge of $g(\omega)$ but using moments of the frequency distribution instead.

Defining the moments as

$$\mu_{2n} = \frac{1}{3N} \int_0^\infty \omega^{2n} g(\omega) \, d\omega$$

when $T > \hbar \omega_{\text{max}}/k_B$ one can write

$$E(T) = 3Nk_B T - 3Nk_B T$$

$$\times \sum_{n=1}^\infty \frac{(-1)^n B_n}{(2n)!} \left( \frac{\hbar}{2k_B T} \right)^{2n} \mu_{2n}$$

where $B_n$ are Bernoulli numbers. First terms in $[64]$ and $[65]$ are classical contributions, the second terms (sums) can be considered as quantum corrections. Taking only the first few terms, $[65]$ takes the following form:

$$C_v(T) \approx 3Nk_B \left[ 1 - \left( \frac{\hbar}{k_B T} \right)^2 \frac{\mu_2}{12} + \left( \frac{\hbar}{k_B T} \right)^4 \frac{\mu_4}{240} ight.$$

$$\left. - \left( \frac{\hbar}{k_B T} \right)^6 \frac{\mu_6}{6048} + \ldots \right]$$

The lowest-order quantum term is, as expected, of order $\hbar^2$.

### 2.06.1.6 Thermodynamic Perturbation Theory

It can be demonstrated (Landau and Lifshitz, 1980) that by modifying the potential energy of the system from $U_0$ to $U_1$ so that $\bar{V} = U_1 - U_0$ is a small perturbation, to first order the free energy becomes

$$F_1 = F_0 + \langle V \rangle_0$$

where subscript '0' means that averaging is performed over the configurations of the unperturbed system. This means that the free energy of a system with the potential $U_1$ can be found by thermodynamic integration from (any) system $U_0$, the free energy of which is known:

$$F_1 = F_0 + \int_{U_0}^{U_1} U \, d\lambda$$

where $U_\lambda = (1-\lambda)U_0 + \lambda U_1$. The same ideas can be used to calculate the free energy profile along the chemical reaction coordinate, or generally the free energy surface – as done in metadynamics simulations (Laio and Parrinello, 2002; Iannuzzi et al., 2003).

To second order, we have

$$F_1 = F_0 + \langle V \rangle_0 - \frac{1}{2k_B T} \langle (V - \bar{V})^2 \rangle_0$$

where $\bar{V}$ is the averaged perturbing potential. Note that the expressions $[67]$ and $[69]$ are classical, but quantum extensions are available (Landau and
Lifshitz, 1980). Thermodynamic perturbation theory plays an important role in methods to calculating free energies.

### 2.06.1.7 Quasiharmonic Approximation

In this approximation, it is assumed that the solid behaves like a harmonic solid at any volume, but the phonon frequencies depend on volume. It is assumed that they depend only on volume—that is, heating at constant volume does not change them.

In the quasiharmonic approximation (QHA) phonons are still independent and noninteracting. Thermodynamic functions at constant volume, as before, are given by $[47]–[50]$, $C_V$ still cannot exceed $3k_B$. Melting, diffusion, and dynamically disordered phases are beyond the scope of this approximation, which breaks down at high temperatures. Thermal conductivity is still infinite.

However crude, this approximation heals the biggest errors of the harmonic approximation. Introducing a volume dependence of the frequencies is enough to create nonzero thermal expansion and account for $C_V < C_P$ [32]. Thermal pressure contributes to all constant-pressure thermodynamic functions (enthalpy $H$, Gibbs free energy $G$, isobaric heat capacity $C_P$, etc.). This is the first approximation to the thermal equation of state of solids, which can be effectively used in conjunction with realistic interatomic potentials (Parker and Price, 1989; Kantorovich, 1995; Gale, 1998) or quantum-mechanical approaches such as density-functional perturbation theory (Baroni et al., 1987, 2001). For instance, using the QHA and calculating phonon frequencies using density-functional theory, Karki and co-authors calculated high-pressure thermal expansion and elastic constants of MgO (Karki et al., 1999) and thermal expansion of MgSiO$_3$ perovskite (Karki et al., 2000). Using similar methodology, Oganov and colleagues calculated a number of mineral phase diagrams—MgO, SiO$_2$, MgSiO$_3$, Al$_2$O$_3$. They found that MgO retains the NaCl-type structure at all conditions of the Earth’s mantle (Oganov et al., 2003) and that phase transitions of SiO$_2$ do not correspond to any observed seismic discontinuities in the mantle (Oganov et al., 2005a).

For MgSiO$_3$ (Oganov and Ono, 2004) and Al$_2$O$_3$ (Oganov and Ono, 2005), new high-pressure ‘post-perovskite’ phases with the CaIrO$_3$-type structure were found to be stable, and their $P$–$T$ stability fields were predicted and, in the same papers, experimentally verified. Also using the QHA and density-functional perturbation theory, Tsuchiya et al. (2004) studied stability of MgSiO$_3$ post-perovskite and confirmed previous experimental (Murakami et al., 2004; Oganov and Ono, 2004) and theoretical (Oganov and Ono, 2004) findings. Oganov and Price (2005) confirmed that MgSiO$_3$ perovskite and post-perovskite remain stable against decomposition at all conditions of the Earth’s mantle, but their decomposition into MgO and SiO$_2$ was predicted to occur at conditions of cores of extraterrestrial giant planets (Umemoto et al., 2006).

### 2.06.1.8 Beyond the QHA

At temperatures roughly below one-half to two-thirds of the melting temperature, QHA is quite accurate. Only at higher temperatures do its errors become significant. All the effects beyond the QHA are known as ‘intrinsic anharmonicity’. For instance, phonon–phonon interactions, displacive phase transitions, and explicit temperature dependence of the vibrational frequencies (which is experimentally measurable) are intrinsic anharmonic phenomena. Here we focus on the role of intrinsic anharmonicity in thermodynamics and equations of state of solids, rather than on aspects related to thermal conductivity and phonon–phonon interactions.

This simplest way of treating intrinsic anharmonicity takes advantage of the fact that in the high-temperature expansion of the anharmonic free energy, the lowest-order term is quadratic (Landau and Lifshitz, 1980; Zharkov and Kalinin, 1971; Gillet et al., 1999). Explicit molecular dynamics simulations for MgO (Figure 4) show that third- and fourth-order terms still play some role, but overall the $T^2$-term dominates. Limiting ourselves to this term, we write

$$
F_{\text{inh}}(V, T) = \frac{1}{3k_B} \frac{\partial^2 F}{\partial V^2} = \frac{1}{2} a T^2
$$

where $a$ is an intrinsic anharmonicity parameter, usually of order $10^{-5}$ K$^{-1}$. Equation [70] assumes that intrinsic anharmonic contributions from different modes are additive. This is clearly a simplification, but it finds some justification in the arguments of Wallace (1998). Intrinsic anharmonicity normally decreases with pressure, which can be accounted for by a simple volume dependence (Zharkov and Kalinin, 1971):

$$
a = a_0 \left( \frac{V}{V_0} \right)^n
$$

where $a_0$ is the intrinsic anharmonicity parameter at zero pressure.
where \( a_0 \) is the intrinsic anharmonicity parameter at standard conditions, and \( m = \left( \frac{\partial \ln a}{\partial \ln V} \right) \) is a constant.

One can easily find other anharmonic thermodynamic properties, such as the entropy, energy, isochoric heat capacity, thermal pressure, and bulk modulus:

\[
\begin{align*}
S_{\text{anh}} &= -aT, \\
E_{\text{anh}} &= -\frac{1}{2} aT^2, \\
C_{V\text{anh}} &= -aT, \\
P_{\text{anh}} &= -\frac{1}{2} \frac{m}{V} T^2, \\
K_{T\text{a}} &= P_a (1 - m)
\end{align*}
\]

This model works well at high temperatures. However, at low temperatures there are problems: linear anharmonic heat capacity \([72]\) overwhelms the harmonic term, leading to large errors in the thermal expansion coefficient below \( \approx 100 \) K. The problem is that \([70]\) and \([72]\) are classical equations and completely ignore quantum vibrational effects, which determine low-temperature thermodynamics.

Wallace (1998) has shown that in the first approximation intrinsic anharmonic effects can be incorporated by using the true (i.e., temperature-dependent) vibrational frequencies \( \omega \) (or characteristic temperatures \( \theta = \frac{\hbar \omega}{k_b} \)) and substituting them into the (quasi)harmonic expression for the entropy for a harmonic oscillator \([45]\). The result will contain both quasiharmonic and intrinsic anharmonic contributions. We follow Gillet et al. (1999) and define the temperature-dependent characteristic temperature as

\[
\Theta_{T} = \theta \exp(aT) \tag{73}
\]

where \( \theta \) is the quasiharmonic (only volume-dependent) characteristic temperature. Equation \([73]\) thus defines the physical meaning of this parameter as the logarithmic derivative of the vibrational frequency (or characteristic temperature) with respect to volume:

\[
a = \left( \frac{\partial \ln \omega}{\partial T} \right)_V = \left( \frac{\partial \ln \Theta_{T}}{\partial T} \right)_V \tag{74}
\]

In the classical limit \( (\Theta_{T}/T \to 0) \) eqns \([70]\) and \([72]\) are easily derived from \([74]\).

Another approach to include quantum corrections in anharmonic properties is offered by thermodynamic perturbation theory of an anharmonic oscillator (see Oganov and Dorogokupets (2004)). Consider a general anharmonic potential

\[
U_i = \frac{1}{2} k x^2 + a_1 x^4 + a_4 x^6 + \cdots \tag{75}
\]

with \( k > 0 \).

As a reference system we take a harmonic oscillator

\[
U_0 = \frac{1}{2} k x^2 \tag{76}
\]

Using first-order thermodynamic perturbation theory \([69]\) anharmonic free energy can be calculated as follows:

\[
F_{\text{anh}} = \langle U - U_0 \rangle_0 = \left( a_1 x^4 + a_4 x^6 + \cdots \right)_0 = a_4 \langle x^4 \rangle_0 + a_6 \langle x^6 \rangle_0 + a_8 \langle x^8 \rangle_0 + \cdots \tag{77}
\]

This expression is remarkable in that the moments of atomic displacements used are those of a harmonic oscillator, and can be easily calculated. Since the harmonic reference potential is symmetric, only even-order terms are retained in \([77]\). Truncating at the \( \langle x^4 \rangle_0 \) term, Oganov and Dorogokupets (2004) found

\[
F_{\text{anh}} = \frac{a}{6 k_b} \left[ \langle F \rangle^2 + 2 k_b C_{V} T^2 \right] \tag{78}
\]

Other thermodynamic functions are easy to derive from \( F_{\text{anh}} \) by differentiation. From \([78]\), one trivially obtains anharmonic zero-point energy:

\[
F_{\text{anh}}^{zp} = \frac{a}{24} k_b \theta^2 \tag{79}
\]

For typical values of parameters \( (a = 2 \times 10^{-5} \ 	ext{K}^{-1}, \ \theta = 1000 \ \text{K}) \), this value amounts to only 0.17% of the harmonic zero-point energy. For more details on this formalism, see Oganov and Dorogokupets (2004).
Computationally, intrinsic anharmonic effects can be fully accounted for by the use of Monte Carlo or molecular dynamics simulations (Allen and Tildesley, 1987); these methods involve a full sampling of the potential hypersurface without any assumptions regarding its shape or the magnitude of atomic vibrations; these methods are also applicable to liquids and gases. Free energies of significantly anharmonic systems can be calculated using thermodynamic integration technique (e.g., Allen and Tildesley, 1987). For example, using this technique Alfè et al. (1999) calculated the melting curve of Fe at conditions of the Earth’s core and provided first-order estimates of core temperatures (more accurate estimates were later obtained taking into account the effects of alloying elements, see Alfè et al. (2002)).

2.06.2 Equations of State and Elasticity

Equations of state (EOSs) (i.e., the P–V–T relationships) of Earth-forming minerals are of special interest – indeed, accurate EOSs of minerals are necessary for the interpretation of seismological observations. The importance of the elastic constants for Earth sciences springs from the fact that most of the information about the deep Earth is obtained seismologically, by measuring the velocities of seismic waves passing through the Earth. Seismic wave velocities, in turn, are related to the elastic constants of Earth-forming rocks and minerals. Acoustic anisotropy of the Earth, measurable seismologically, is related to the elastic anisotropy of Earth-forming minerals and the degree of their alignment.

2.06.2.1 Equations of State

Generally, thermodynamics gives

\[ P = -\left(\frac{\partial F}{\partial V}\right)_T \]  and  \[ V = \left(\frac{\partial G}{\partial P}\right)_T \] (Isothermal EOS)

\[ T = \left(\frac{\partial H}{\partial S}\right)_p \]  and  \[ S = -\left(\frac{\partial G}{\partial T}\right)_p \] (Isobaric EOS)

\[ P = -\left(\frac{\partial F}{\partial V}\right)_S \]  and  \[ V = -\left(\frac{\partial H}{\partial P}\right)_S \] (Adiabatic EOS)

An explicit analytical EOS can only be written for an ideal gas (where interatomic interactions are absent; in the case, there are no problems in the analytical representation of the interatomic potential, and entropy can be easily and exactly calculated using the Sackur–Tetrode relation). For solids and liquids interatomic interactions are essential, and all existing analytical EOSs are by necessity approximate. Even worse, interactions between atoms make phase transitions possible, and EOS becomes discontinuous (i.e., nonanalytical) at phase transitions. All the approximate EOS formulations are valid only for one phase (though for a phase transition involving only small structural changes it is possible to formulate a single EOS describing two or more phases – see, e.g., Tröster et al. (2002)), and generally the accuracy of the EOS is best at conditions far from phase transitions.

2.06.2.1.1 Mie–Grüneisen EOS

To advance further, consider the isothermal EOS \[ P = -\left(\frac{\partial F}{\partial V}\right)_T \], taking the QHA as the starting point. Using indices i and k to denote the number of the phonon branch and the wave vector k, we can write a formula analogous to [50]:

\[ F(T) = E_0 + \frac{1}{2} \sum_{i,k} \hbar \omega_i \]

\[ + k_B T \sum_{i,k} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_i}{k_B T} \right) \right] \]  \[ \text{[80]} \]

From this, we have

\[ P(V, T) = P_{st}(V) + \frac{1}{2} \sum_{i,k} \gamma_i \frac{\hbar \omega_i}{V} \]

\[ + \sum_{i,k} \frac{\gamma_i}{V} \right) \exp \left( \frac{\hbar \omega_i}{k_B T} \right) - 1 \]  \[ \text{[81]} \]

where \( P_{st}(V) \) is the static pressure, and the mode Grüneisen parameter \( \gamma_i \) is defined as

\[ \gamma_i = \left( \frac{\partial \ln \omega_i}{\partial \ln V} \right)_T \]  \[ \text{[82]} \]

In the QHA, the Grüneisen parameter is temperature independent.

At high temperatures or when all \( \gamma_i \) are equal, \[ \text{[81]} \] can be simplified:

\[ P(V, T) = P_{st}(V) + \frac{E_{\text{ vib}}(V, T)}{V} \]  \[ \text{[83]} \]

where

\[ \gamma = \left\{ \gamma_i \right\} \]  \[ \text{[84]} \]

Equation \[ \text{[83]} \] is the famous Mie–Grüneisen thermal EOS. It should be noted that in the classical approximation, which is put in the basis of the standard molecular dynamics and Monte Carlo simulations, the thermodynamic Grüneisen parameter
will always be close to $<\gamma_{ik}>$ (Welch et al., 1978), but it will also include a temperature-dependent correction due to intrinsic anharmonic effects.

As shown by Holzapfel (2001), the three common definitions of the Grüneisen parameter (via the thermal pressure, thermal expansion, and volume derivatives of the phonon frequencies)

$$\gamma_p(V, T) = \frac{P_{\text{th}}}{E_{\text{th}}} V$$ \[85a\]

$$\gamma_\alpha(V, T) = \frac{K_T V}{C_V}$$ \[85b\]

$$\gamma_{qh}(V) = \left\langle \frac{-\partial \ln \omega}{\partial \ln V} \right\rangle$$ \[85c\]

are all identical for a classical quasiharmonic solid, and all different for a system with intrinsic anharmonicity. Very roughly, $\gamma_p(V, T)$ is halfway between $\gamma_{qh}(V)$ and $\gamma_\alpha(V, T)$, that is, anharmonic effects are much pronounced in thermal expansion than in thermal pressure. We stress that care must be taken as to which definition of the Grüneisen parameter is used when analyzing experimental and theoretical results. Figure 5 shows the different definitions of the Grüneisen parameter and that the differences are small at low temperatures, but significantly increase with temperature; also shown is the volume dependence of the parameter $q$:

$$q = \left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T$$ \[86\]

Often, the volume dependence of $\gamma$ is described by a power law:

$$\gamma(V) = \gamma_0 \left( \frac{V}{V_0} \right)^q$$ \[87\]

where parameter $q$ is usually assumed to be constant. However, this form becomes poor at high compression. A much better function was proposed by Al’tshuler et al. (1987) (see also Vorobev (1996)):

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) \left( \frac{V}{V_0} \right)^q$$ \[88\]

where $\gamma_0$ and $\gamma_\infty$ are Grüneisen parameters at $V = V_0$ and at infinite compression ($V = 0$), respectively.

### 2.06.2.1.2 Analytical static EOS

Good discussions of this issue can be found in many sources, including Holzapfel (1996, 2001), Sutton (1993), Hama and Suito (1996), Cohen et al. (2000), Poirier (2000), and Vinet et al. (1986, 1989). Over the decades, many different EOS forms have been generated, but here we discuss only the ones that are most interesting from the theoretical and practical points of view.

The simplest approach is based on elasticity theory. Assuming that the bulk modulus $K$ varies linearly with pressure and denoting $K_0 = (\partial K/\partial P)_{P=0}$, we obtain the Murnaghan EOS:

$$P = \frac{K_0}{K_0} \left( \frac{V}{V_0} \right)^{-\frac{K_0}{K_0}} - 1$$ \[89\]

Figure 5 Grüneisen parameters and $q$ parameters of MgO as a function of volume. (a) At 300 K, (b) at 3000 K. Solid lines indicate quasiharmonic results, dotted lines (middle) indicate $\gamma_p$, dashed lines indicate $\gamma_\alpha$. From Oganov AR and Dorogokupets PI (2003) All-electron and pseudopotential study of MgO: Equation of state, anharmonicity, and stability. Physical Review B67 (uppermost for $\gamma$ and $q$) (art. 224110).
This simple EOS works reasonably well only in a very limited compression range. A better approach (in terms of the accuracy relative to the number of parameters of the mathematical formulation) is provided by the effective potential methods, where an approximate model for the energy as a function of \( x = V/V_0 \), or some other measure of strain, is used.

For example, starting from a polynomial

\[
E = E_0 + af^2 + bf^3 + cf^4 + \cdots
\]

in terms of the Eulerian strain \( f \): \( f = (1/2)[x^{2/3} - 1] \), one arrives at the family of Birch–Murnaghan EOSs. (It is advantageous to use the Eulerian finite strain rather than the Lagrangian strain \( f_l = (1/2)[1 - x^{2/3}] \), because the Eulerian strain leads to a better description of the correct \( E(V) \) dependence with fewer terms in the expansion [90]. At infinite pressure, Eulerian strain is infinite, whereas Lagrangian strain remains finite and will require an infinite-order expansion. However, for infinitesimal strains both definitions become equivalent.) The often used third-order Birch–Murnaghan EOS is

\[
P = \frac{3}{2} K_0 \left[ x^{7/3} - x^{5/3} \right] \left\{ 1 + \xi \left[ x^{2/3} - 1 \right] \right\}
\]

\[
E = E_0 + \frac{3}{2} K_0 V_0 \left[ \frac{3}{2} (\xi - 1) x^{-2/3} + \frac{3}{4} (1 - 2\xi) x^{-4/3} \right] + \frac{1}{2} \xi x^{-6/3}
\]

\[
\frac{2\xi - 3}{4}
\]

where \( \xi = (3/4) (K_0 - 4) \).

It is possible to derive systematically higher-order BM EOSs, but this appears to be of little use since the number of parameters involved becomes too large; only the fourth-order BM EOS

\[
P = 3K_0 f_c (1 + 2f_c)^{5/2} \left\{ 1 + \frac{3}{2} (K_0 - 4)f_c \right\}
+ \frac{3}{2} \left[ K_0 k_0^3 + (K_0 - 4)(K_0 - 3) + \frac{35}{8} \right] f_c^3 \}
\]

is sometimes used when ultrahigh pressures are studied.

The Vinet EOS (Vinet et al., 1986, 1989) is sometimes considered as one of the most impressive recent achievements in solid-state physics (Sutton, 1993). In fact, this is a whole family of EOSs of different orders. The most remarkable feature is its very fast convergence with respect to the order of EOS—one seldom needs to use beyond the third-order Vinet EOS.

This EOS is based on a universal scaled binding energy curve

\[
E = E_0(1 + a) \exp(-a)
\]

where \( E_0 \) is the bond energy at equilibrium, \( a = (R - R_0)/l \), \( l = \sqrt{E_0/(\tilde{V}^2 E_0/R^2)} \) being a scaling length roughly measuring the width of the potential well, and \( R \) the Wigner–Seitz radius (the average radius of a sphere in the solid containing one atom). The potential [94] was invented and first used by Rydberg (1932) for fitting potential curves of molecules and obtaining their anharmonic coefficients; it turned out (Vinet et al., 1986) that it describes very accurately systems with different types of chemical bonding in solids, molecules, adsorbates, etc.

The third-order Vinet EOS is (Vinet et al., 1989; Hama and Suito, 1996)

\[
P = 3K_0 (1 - x^{1/3})^2 \exp(\eta(1 - x^{1/3}))
\]

\[
E(V) = E(V_0) + \frac{9K_0 V_0}{\eta^2} \left\{ 1 - \eta(1 - x^{1/3}) \right\}
\]

\[
\times \exp(\eta(1 - x^{1/3})) \}
\]

where \( \eta = (3/2)(K_0 - 1) \). The resulting expression for the bulk modulus is

\[
k = \frac{K_0 x^{2/3}(1 + (1 + \eta x^{1/3})(1 - x^{1/3})) \exp(\eta(1 - x^{1/3}))}{\frac{4}{3}}
\]

From this one has (Vinet et al., 1989)

\[
k_0^\eta = -\frac{1}{K_0} \left[ \left( \frac{K_0}{2} \right)^2 + \frac{K_0}{2} - \frac{19}{36} \right]
\]

The Vinet EOS proved to be very accurate for fitting EOS of solid hydrogen (Loubeyre et al., 1996; Cohen et al., 2000) throughout the whole experimentally studied pressure range 0–120 GPa, roughly to the eightfold compression.

In very rare cases a higher-order Vinet EOS may be needed; such higher-order versions of the Vinet EOS already exist (Vinet et al., 1989):

\[
P = \frac{3}{2} K_0 (1 - x^{1/3})^2 \exp(\eta(1 - x^{1/3})) + \beta(1 - x^{1/3})^3
\]

\[
+ \gamma(1 - x^{1/3})^4 + \cdots
\]

\[
(36K_0)^2 + 9K_0^2 + 18K_0^2 - 19) \gamma = 0, \text{ has been}
\]

successfully applied to solid H$_2$ at extreme compressions (Cohen et al., 2000) and has led to significant improvements of the description of experimental \( PV \)-data.
In the limit of extreme compressions \((x \to 0)\) the Vinet EOS fails to reproduce the correct free-electron limit and gives a finite (rather than positive infinite) energy equal to \((9K_0V_0/\eta^9)[1-(1-\eta)\exp(\eta)]\) (we do not consider here nuclear forces, which become important at densities \(\sim 10^{15} \text{ g cm}^{-3}\) \((P \sim 10^{20} \text{ GPa})\) corresponding to \(x < 10^{-12}\) (Holzapfel, 2001)). EOSs, manifesting the correct Thomas–Fermi behavior at extreme compressions, have been developed and discussed in detail by Holzapfel (1996, 2001) and Hama and Suito (1996).

Holzapfel (1996, 2001) has modified the Vinet EOS so as to make it satisfy the electron-gas limit at extreme compressions. His APL EOS (also a family of \(L\)th-order EOSs) is as follows (Holzapfel, 2001):

\[
P = \frac{3K_0}{x^{3/2}}(1-x^{1/3})\exp[\epsilon_0(1-x^{1/3})] \\
\times \left\{1 + x^{1/3} \sum_{k=2}^{L} \epsilon_k(1-x^{1/3})^{k-1}\right\} \tag{100}
\]

where \(\epsilon_0 = -\ln(3K_0/P_{FG0})\), \(P_{FG0} = a_{FG}(Z/V_0)^{3/2}\), \(a_{FG}=0.02337 \text{ GPa Å}^{-5}\), and \(Z\) the total number of electrons per volume \(V_0\).

This EOS correctly predicts that at infinite compression \(K'_\infty = 5/3\) (while at \(x = 1\) \(K'_0 = 3 + (3/2)(\epsilon_0 + \epsilon_2)\)), but becomes very similar to the Vinet EOS at moderate compressions. The mathematical similarity between [99] and [100] is obvious, and it is easy to generalize these EOSs into one family. For a third-order generalized Vinet–Holzapfel EOS, one has (Kunc et al., 2003)

\[
P = \frac{3K_0}{x^{3/2}}(1-x^{1/3})\exp[\epsilon_0(1-x^{1/3})] \tag{101}
\]

where \(\eta = (3K_0/2) + (1/2) - n\). The Vinet EOS is recovered when \(n = 2\), and the Holzapfel EOS is obtained when \(n = 5\). Kunc et al. (2003) found that theoretical EOS of diamond is best represented by the EOS [101] with an intermediate value \(n = 7/2\). In this case, the energy can be expressed analytically:

\[
E(V) = E(V_0) + 9K_0V_0[f(V) - f(V_0)]\exp(\eta) \sqrt{\eta} \tag{102}
\]

where

\[
f(V) = \sqrt{\pi}(2n+1)\text{erf}(\sqrt{\eta x^{1/3}}) + \left(\frac{2\sqrt{\eta} \exp(-\eta x^{1/3})}{x^{1/3}}\right)
\]

However, it remains to be seen how accurate [102] is for other materials.

### 20.06.2.1.3 Anharmonicity in static EOS

Since both \(K'\) and \(\gamma\) come from anharmonic interactions, an intriguing possibility arises to establish a general relation between these parameters. This possibility has been widely discussed since 1939, when J. Slater suggested the first solution of the problem:

\[
\gamma_s = \frac{1}{2} K - \frac{1}{6} \tag{103}
\]

Later approaches resulted in very similar equations, the difference being in the value of the constant subtracted from \((1/2) K': 1/2, 5/6, \text{ or } 0.95\). If any of the relations of the type [103] were accurate, it would greatly simplify the construction of thermal EOS. Although some linear correlation between \(\gamma\) and \(K'\) does exist, the correlation is too poor to be useful (Wallace, 1998; Vočadlo et al., 2000).

### 20.06.2.1.4 EOS, internal strain, and phase transitions

All the EOSs discussed in the previous section implicitly assumed that crystal structures compress uniformly, and there is no relaxation of the unit cell shape or of the atomic positions. For some solids (e.g., MgO) this is definitely true. For most crystals and all glasses, however, this is an approximation, sometimes crude. Classical EOSs are less successful for crystals with internal degrees of freedom and perform particularly poorly in the vicinity of phase transitions. In the simplest harmonic model, Oganov (2002) obtained the following formula:

\[
P(V) = P_{\text{unrelaxed}}(V) + \sum_i m_i^2(V - V_0) \tag{104}
\]

with parameters \(m_i\). \(P_{\text{unrelaxed}}\) is well described by the conventional EOSs, for example, Vinet EOS, whereas the total EOS is not necessarily so (see line 2 in Figure 6). The bulk modulus is always lowered by the relaxation effects, in the simplest approximation [104]:

\[
K(V) = K_{\text{unrelaxed}}(V) - \sum_i m_i^2 V \tag{105}
\]

which implies the tendency of \(K'\) to be higher than the corresponding unrelaxed value:

\[
K'(V) = K'_{\text{unrelaxed}}(V) + \sum_i m_i^2 \frac{V}{K} \tag{106}
\]

This simple model explains qualitatively correctly the real effects of internal strain. Complex structures are usually relatively ‘soft’ and usually have large \(K'_0\).
Figure 6  Effects of internal strains on equation of state. At the highest pressures shown, the structure is on the verge of an isosymmetric phase transition. 1, unrelaxed EOS; 2, correct EOS including relaxation; 3, the difference caused by relaxation. Note that in the pretransition region the full EOS is poorly fit, while the unrelaxed EOS is very well represented by analytical EOSs (in this case BM3).

(often significantly exceeding ‘normal’ $K_0 = 4$), in agreement with the prediction [106]. For example, quartz SiO$_2$, although consisting of extremely rigid SiO$_2$ tetrahedra, has a very low bulk modulus $K_0 = 37.12$ GPa and high $K_0' = 5.99$ (Angel et al., 1997): its structure is very flexible due to relaxation of the internal degrees of freedom. Perhaps, the highest known $K_0' = 13$ was found in amphibole grunerite (Zhang et al., 1992) with a very complicated structure having many degrees of freedom.

As an illustration, consider two series of ab initio calculations on sillimanite, Al$_2$SiO$_5$ (based on results from Oganov et al. (2001b)). In one series all structural parameters were optimized, while in the other series the zero-pressure structure was compressed homogeneously (i.e., without any relaxation). Results are shown in Figure 6, where a very large relaxation effect can be seen.

It is well known that internal strains always soften the elastic constants (e.g., Catti, 1989). In extreme cases, the softening can be complete, leading to a phase transition. In such cases, the simplified model [104] is not sufficient. To study EOS in the vicinity of the phase transition, one needs to go beyond the harmonic approximation built in this model. This can be done using the Landau expansion of the internal energy in powers of $Q$ including the full elastic constants tensor and allowed couplings of the order parameter and lattice strains (see, e.g., Tröster et al. (2002)).

2.06.2.2 Elastic Constants

A number of excellent books and reviews exist, especially, Nye (1998), Sirotin and Shaskolskaya (1975), Wallace (1998), Alexandrov and Prodaïova (1993), Born and Huang (1954), Belikov et al. (1970), Barron and Klein (1965), and Fedorov (1968).

Elastic constants characterize the ability of a material to deform under small stresses. They can be described by a fourth-rank tensor $C_{ijkl}$ relating the second-rank stress tensor $\sigma_{ij}$ to the (also second-rank) strain tensor $\varepsilon_{ij}$ via the generalized Hooke’s law:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}$$  \[107\]

where multiplication follows the rules of tensor multiplication (see Nye, 1998). Equation [107] can be simplified using the Voigt notation (Nye, 1998), which represents the fourth-rank tensor $C_{ijkl}$ by a symmetric $6 \times 6$ matrix $C_{ij}$. In these notations, indices ‘11’, ‘22’, ‘33’, ‘12’, ‘13’, ‘23’ are represented by only one symbol $= 1, 2, 3, 6, 5, 4$, respectively. So we write instead of [107]

$$\sigma_i = C_{ij} \varepsilon_j$$  \[108\]

Note that infinitesimal strains are being used; in this limit, all definitions of strain (e.g., Eulerian, Lagrangian, Hencky, etc.) become equivalent. Under a small strain, each lattice vector $a_{ij}$ of the strained crystal is obtained from the old lattice vector $a_{ij}^0$ and the strain tensor $\varepsilon_{ij}$ using the relation

$$a_{ij}' = (\delta_{ij} + \varepsilon_{ij})a_{ij}^0$$  \[109\]

In the original tensor notation and in the Voigt notation (Nye, 1998), the $(\delta_{ij} + \varepsilon_{ij})$ matrix is represented as follows:

$$\begin{bmatrix} 1 + \varepsilon_1 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 \\ \varepsilon_1 & 1 + \varepsilon_2 & \varepsilon_2 & \varepsilon_3 \\ \varepsilon_2 & \varepsilon_2 & 1 + \varepsilon_3 & \varepsilon_3 \\ \varepsilon_3 & \varepsilon_3 & \varepsilon_3 & 1 + \varepsilon_3 \end{bmatrix} = \begin{bmatrix} 1 + \varepsilon_1 & \varepsilon_6 / 2 & \varepsilon_6 / 2 \\ \varepsilon_6 / 2 & 1 + \varepsilon_2 & \varepsilon_4 / 2 \\ \varepsilon_6 / 2 & \varepsilon_4 / 2 & 1 + \varepsilon_1 \end{bmatrix}$$  \[110\]

Voigt notation is sufficient in most situations; only in rare situations such as a general transformation of the coordinate system, the full fourth-rank tensor representation must be used to derive the transformed elastic constants.

The number of components of a fourth-rank tensor is 81; the Voigt notation reduces this to 36. The thermodynamic equality $C_{ij} = C_{ji}$ makes the $6 \times 6$
matrix of elastic constants symmetric, reducing the
number of independent constants to the well-known
maximum number of 21, possessed by triclinic crys-
tals. Crystal symmetry results in further reductions of
this number: 13 for monoclinic, 9 for orthorhombic, 6
or 7 (depending on the point group symmetry) for
trigonal and tetragonal, 5 for hexagonal, and 3 for
cubic crystals; for isotropic (amorphous) solids there
are only two independent elastic constants.

One can define the inverse tensor \( S_{ij}^{-1} \) (or, in the
Voigt notation, \( S_{ij} \)), often called the elastic compli-
tance tensor:

\[
\{ S_{ij} \} = \{ C_{ij} \}^{-1} \quad \text{or} \quad \{ S_{ij} \} = \{ C_{ij} \}^{-1}
\]

(Note that in Voigt notation \( C_{ijkl} = C_{mm} \) but \( S_{ijkl} = S_{mm} \)
only when \( m = 1, 2, \) or 3; when either \( m \) or \( n = 4, 5, \) or 6: 2 \( S_{ijkl} = S_{mm} \); when both \( m \) and \( n = 4, 5, \) or 6: 4 \( S_{ijkl} = S_{mm} \) (Nye, 1998).) The \( S_{ij} \) tensor can be
defined via the generalized Hooke’s law in its equiv-
alent formulation:

\[
\varepsilon_i = S_{ij} \sigma_j
\]

Linear compressibilities can be easily derived
from the \( S_{ij} \) tensor. Full expressions for an arbitrary
direction can be found in Nye (1998); along the
coordinate axes, the linear compressibilities are

\[
\begin{align*}
\beta_x &= - \frac{1}{l_x} \left( \frac{\partial \varepsilon}{\partial \sigma} \right)_T = \sum_{j=1}^{3} S_{ij} = S_{11} + S_{12} + S_{13} \\
\beta_y &= - \frac{1}{l_y} \left( \frac{\partial \varepsilon}{\partial \sigma} \right)_T = \sum_{j=1}^{3} S_{ij} = S_{12} + S_{22} + S_{23} \quad [113] \\
\beta_z &= - \frac{1}{l_z} \left( \frac{\partial \varepsilon}{\partial \sigma} \right)_T = \sum_{j=1}^{3} S_{ij} = S_{13} + S_{23} + S_{33}
\end{align*}
\]

where \( l_x, l_y, l_z \) are linear dimensions along the axes of
the coordinate system. (These axes may not coincide
with the lattice vectors for nonorthogonal crystal
systems. Coordinate systems used in crystal physics
are always orthogonal.) For the bulk compressibility, we
have

\[
\beta = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \beta_x + \beta_y + \beta_z = \sum_{j=1}^{3} \sum_{j=1}^{3} S_{ij} = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})
\]

The values of the elastic constants depend on the
orientation of the coordinate system. There are two
particularly important invariants of the elastic con-
stants tensor – bulk modulus \( K \) and shear modulus \( G \),
obtained by special averaging of the individual elastic
constants. There are several different schemes of
such averaging. Reuss averaging is based on the
assumption of a homogeneous stress throughout
the crystal, leading to the Reuss bulk modulus:

\[
K_R = \frac{1}{S_{11} + S_{12} + S_{13} + 2(S_{12} + S_{13} + S_{23})} = \frac{1}{\beta} \quad [115]
\]

and shear modulus:

\[
G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})}
\]

It is important to realize that it is the Reuss bulk
modulus, explicitly related to compressibility, that
is used in constructing EOSs and appears in all ther-
mododynamic equations involving the bulk modulus.

Another popular scheme of averaging is due to
Voigt. It is based on the assumption of a spatially
homogeneous strain, and leads to the following
expressions for the Voigt bulk and shear moduli:

\[
\begin{align*}
K_V &= \frac{C_{11} + C_{22} + C_{33} + 2(C_{13} + C_{13} + C_{23})}{9} \quad [117] \\
G_V &= \frac{C_{11} + C_{22} + C_{33} + (C_{13} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})}{15} \quad [118]
\end{align*}
\]

For an isotropic polycrystalline aggregate the Voigt
moduli give upper and the Reuss moduli lower bounds
for the corresponding moduli. More accurate estimates
can be obtained from Voigt–Reuss–Hill averages:

\[
K_{VRH} = \frac{K_V + K_R}{2}, \quad G_{VRH} = \frac{G_V + G_R}{2} \quad [119]
\]

The most accurate results (and tighter bounds) are
given by the Hashin–Shtrikman variational scheme,
which is much more complicated, but leads to results
similar to the Voigt–Reuss–Hill scheme (see Watt
et al. (1976) for more details).

There are two groups of experimental methods
for measuring the elastic constants: (1) static and
low-frequency methods (based on determination of
stress–strain relations for static stresses) and (2) high-
frequency or dynamic methods (e.g., ultrasonic
methods and Brillouin spectroscopy). High-
frequency methods generally enable much higher
accuracy. Static measurements yield isothermal elas-
tic constants (the timescale of the experiment allows
thermal equilibrium to be attained within the sam-
ple); high-frequency measurements give adiabatic
Acoustic velocities as a function of the 

density of the crystal. It can also be repre-

dented in the form of a secular equation:

\[ K_s = K_T (1 + \alpha \gamma T) = K_T \left( 1 + \frac{\alpha^2 K_T V}{C_V} \right) \]

where \( \alpha \) and \( \gamma \) are the thermal expansion and

\[ \text{Grüneisen parameter, respectively. Adiabatic and} \]

isothermal shear moduli are strictly equal for cubic

\[ \text{crystals and usually practically indistinguishable for} \]

crystals of other symmetries.

Acoustic wave velocities measured in seismologi-

cal experiments and ultrasonic determinations of

\[ \text{elastic constants are related to the adiabatic elastic} \]

constants (Belikov \textit{et al}, 1970). The difference, which

is entirely due to anharmonic effects (see below),

vanishes at 0 K. Adiabatic \( C_{ij} \) are larger, usually by a

few percent. The following thermodynamic equation

gives the difference in terms of thermal pressure

tensor \( b_{ij} \) (Wallace, 1998):

\[ c_{ijkl}^S = c_{ijkl}^V + \frac{T}{C_V} b_{ij} b_{kl} \]  \[ \text{[120]} \]

where \( b_{ij} = \left( \partial \sigma_{ij} / \partial T \right)_V \) is related to the thermal

expansion tensor. Equation [120] implies, for the

bulk moduli, the already-mentioned formula [33]:

\[ K_s = K_T (1 + \alpha \gamma T) = K_T \left( 1 + \frac{\alpha^2 K_T V}{C_V} \right) \]

\[ \text{where} \ \alpha \ \text{and} \ \gamma \ \text{are the thermal expansion and} \]

\[ \text{Grüneisen parameter, respectively. Adiabatic and} \]

isothermal shear moduli are strictly equal for cubic

\[ \text{crystals and usually practically indistinguishable for} \]

crystals of other symmetries.

Acoustic wave velocities measured in seismologi-

cal experiments and ultrasonic determinations of

\[ \text{elastic constants are related to the adiabatic elastic} \]

constants. Isothermal constants, on the other hand,

are related to the compressibility and EOS.

The general equation for the calculation of velo-

cities of acoustic waves with an arbitrary propagation

direction, the Christoffel equation (Sirotin and

Shaskolskaya, 1975), is

\[ c_{ijkl}^S \mathbf{m}_i \mathbf{m}_j \rho_i = \rho \mathbf{v}_i \rho_i \]  \[ \text{[121]} \]

where \( \rho \) is the polarization vector of the wave (of unit

length), \( \mathbf{m} \) the unit vector parallel to the wave vector, and

\( \rho \) the density of the crystal. It can also be repre-

dented in the form of a secular equation:

\[ \det \left| c_{ijkl}^S \mathbf{m}_j \mathbf{m}_k - \rho \mathbf{v}_\mathbf{i} b_{i\mathbf{j}} \right| = 0 \]  \[ \text{[122]} \]

This equation has three solutions, one of which cor-

responds to a longitudinal, and the other two to

transverse waves (see, e.g., Figure 7). For example,

one can obtain the following velocities for a cubic

crystal along high-symmetry directions:

\( \mathbf{m} = [100] \):

\[ v_1 = \sqrt{\frac{\mathbf{C}_{11}}{\rho}} (\mathbf{p} = [100]) \]

\[ v_2 = \sqrt{\frac{\mathbf{C}_{14}}{\rho}} (\mathbf{p} = [010]) \]

\[ v_3 = \sqrt{\frac{\mathbf{C}_{14}}{\rho}} (\mathbf{p} = [001]) \]

\[ \text{The average velocities are given by famous equa-} \]

tions (Belikov \textit{et al}, 1970)

\[ v_p = \sqrt{\frac{5K + 4G}{3\rho}} \]  \[ \text{[123]} \]

and

\[ v_s = \sqrt{\frac{G}{\rho}} \]  \[ \text{[124]} \]

where the adiabatic Voigt–Reuss–Hill (or Hashin–

Shtrikman) values are used for the bulk and shear

moduli.

At constant \( P, T \), the elastic constants describing

stress–strain relations [107] are given by

\[ C_{ijkl}^T = \frac{1}{V} \left( \frac{\partial^2 G}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)_T \]  \[ \text{[125]} \]

while at constant \( P, S \), they are

\[ C_{ijkl}^S = \frac{1}{V} \left( \frac{\partial^2 H}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)_S \]  \[ \text{[126]} \]
Now let us derive from [125] an expression for the elastic constants in terms of the second derivatives of the internal energy; in this derivation, we follow Ackland and Reed (2003). The unit cell of a crystal can be represented by a matrix $\mathbf{V} = (a_1, a_2, a_3)$, and the volume of the equilibrium unit cell is then $V_0 = \det \mathbf{V}$. Using [109], for the volume $V$ of a strained cell we obtain

$$\frac{V}{V_0} = 1 + \epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l + \epsilon_m + \epsilon_n + \epsilon_o$$

Then one has in the standard tensor notation

$$\frac{\Delta V}{V_0} = C_{ij} + \frac{1}{4} (2\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk}) C_{kl} e_{il} + O(e^3)$$

Then, the change of the Gibbs free energy associated with strain is, to the second order,

$$\Delta G = \Delta F + P e_i + \frac{PV}{4} (2\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk}) e_{ij} e_{kl}$$

From this one has

$$C_{ijkl}^T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial \epsilon_i \partial \epsilon_j} \right) + \frac{P}{2} (2\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk})$$

and, by analogy,

$$C_{ijkl}^S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial \epsilon_i \partial \epsilon_j} \right) + \frac{P}{2} (2\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk})$$

It is well known (Barron and Klein, 1965; Wallace, 1998) that under nonzero stresses there can be several different definitions of elastic constants. The constants $C_{ijkl}^T$ and $C_{ijkl}^S$ defined by eqns [130a] and [130b] are those appearing in stress–strain relations and in the conditions of mechanical stability of crystals (see below), whereas the long-wavelength limit of lattice dynamics is controlled by

$$\frac{1}{V} \left( \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \right)$$

These two definitions (via stress–strain relations and from long-wavelength lattice dynamics) become identical at zero pressure.

Calculating the second derivatives with respect to the finite Lagrangian strains $\eta_\gamma$, different equations are obtained (Wallace, 1998) for the case of hydrostatic pressure:

$$C_{ijkl}^T = \frac{1}{V} \left( \frac{\partial^2 E}{\partial \eta_i \partial \eta_j} \right) + P (\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk})$$

$$C_{ijkl}^S = \frac{1}{V} \left( \frac{\partial^2 E}{\partial \eta_i \partial \eta_j} \right) + P (\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk})$$

For a general stress the analogous equations are

$$C_{ijkl}^T = \frac{1}{V} \left( \frac{\partial^2 E}{\partial \eta_i \partial \eta_j} \right) + P (\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{il} \delta_{jk})$$

Cauchy relations, originally derived with the definition via the energy density, can be elegantly formulated in this definition as well (see below). Note, however, that the elastic constants $C_{ijkl}$ defined from stress–strain relations, have the full Voigt symmetry only at hydrostatic pressure. It is essential to distinguish between different definitions of elastic constants under pressure.

### 2.06.2.2.1 Cauchy relations

For crystals where all atoms occupy centrosymmetrical positions, and where all interatomic interactions are central and pairwise (i.e., depend only on the distances between atoms, and not on angles), in the static limit Cauchy relations (Born and Huang, 1954; but take into account eqns [130a] and [130b]) hold:

$$C_{21} = C_{44} = 2P; C_{11} - C_{55} = 2P; C_{12} - C_{66} = 2P$$

$$C_{14} - C_{46} = 0; C_{25} - C_{64} = 0; C_{36} - C_{45} = 0$$

These relations would reduce the maximum number of independent elastic constants to 15; however, they never hold exactly because there are always noncentral and many-body contributions to crystal energy. Violations of the Cauchy relations can serve as a useful indicator of the importance of such interactions. While for many alkali halides Cauchy relations hold reasonably well, for alkali earth oxides (e.g., MgO) they are grossly violated. This is because the free $O^{2-}$ ion is unstable and can exist only in the crystalline environment due to the stabilizing Madelung potential created by all atoms in the crystal; the charge density around $O^{2-}$ is thus very susceptible to the changes of structure,
including strains. Consequently, interactions of the \( \mathrm{O}^{2-} \) ion with any other ion depend on the volume of the crystal and location of all other ions; this is a major source of many-body effects in ionic solids. This point of view is strongly supported by the success of potential induced breathing (PIB, see Bukowski (1994) and references therein) and similar models in reproducing the observed Cauchy violations. In these models, the size of an \( \mathrm{O}^{2-} \) ion (more precisely, the radius of the Watson sphere stabilizing the \( \mathrm{O}^{2-} \)) depends on the classical electrostatic potential induced by other ions.

### 2.06.2.2.2 Mechanical stability

One of the most common types of instabilities occurring in crystals is the so-called mechanical instability, when some of the elastic constants (or their special combinations) become zero or negative. The condition of mechanical stability is the positive definiteness of the elastic constants matrix:

\[
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{bmatrix}
\]

This is equivalent to positiveness of all the principal minors of this matrix (principal minors are square submatrices symmetrical with respect to the main diagonal – they are indicated by dashed lines in the scheme above). All diagonal elastic constants \( C_{ii} \) are principal minors, and, therefore, must be positive for all stable crystals. Mechanical stability criteria were first suggested by Max Born (Born and Huang, 1954) and are sometimes called Born conditions. In general form, they are analyzed in detail in Sirotin and Shaskolskaya (1982) and Fedorov (1968), and cases of different symmetries have been thoroughly analyzed by Cowley (1976) and by Terhune et al. (1985). Mechanical stability criteria for crystals under stress must employ the \( C_{ii} \) derived from the stress–strain relations (Wang et al., 1993, 1995; Karki, 1997). Violation of any of the mechanical stability conditions leads to softening of an acoustic mode in the vicinity of the \( \Gamma \)-point, inducing a phase transition.

### 2.06.2.2.3 Birch’s law and effects of temperature on the elastic constants

The famous Birch’s law (Birch, 1952, 1961; Poirier, 2000) states that compressional sound velocities depend only on the composition and density of the material:

\[
v_p = a(M) + b(M) \rho \tag{134}
\]

where \( \dot{M} \) is the average atomic mass, \( a \) and \( b \) constants, \( \rho \) the density. Thus, for the mantle materials (average atomic mass between 20 and 22),

\[
v_p = -1.87 + 3.05 \rho \tag{135}
\]

Similar relations hold for the bulk sound velocity \( v_B = \sqrt{K/\rho} \) for mantle compositions

\[
v_B = -1.75 + 2.36 \rho \tag{136}
\]

Birch’s law implies that for a given material at constant volume, the elastic constants are temperature independent. This can be accepted only as a first (strictly harmonic) approximation. Thermal contributions to the bulk modulus can be represented as additive corrections to the zero-temperature result:

\[
K^T(V, T) = K_0 K(V) + \Delta K^T_{\text{hqa}}(V, T) + \Delta K^T_{\text{s}}(V, T) \tag{137}
\]

\[
\Delta K^T_{\text{hqa}}(V, T) = \rho_{\text{hqa}}(1 + \gamma - q) - \gamma^2 TC_V/V \tag{138}
\]

\[
\Delta K^T_{\text{s}}(V, T) = \rho_s (1 + \gamma - q_s) \tag{139}
\]

where

\[
\rho_s = \rho_s E_s / V, \quad \gamma_s = -\frac{\partial \ln a}{\partial \ln V}, \quad q_s = \frac{\partial \ln \gamma_s}{\partial \ln V}
\]

For the adiabatic bulk modulus

\[
K^\beta(V, T) = K_0 K(V) + \rho_{\text{hqa}}(1 + \gamma - q) + \rho_s (1 + \gamma - q_s) \tag{140}
\]

These results can be generalized for the individual elastic constants. Garber and Granato (1975), differentiating the free energy, expressed in the QHA as a sum of mode contributions over the whole Brillouin zone:

\[
F = E_{\text{el}} + \frac{1}{2} \sum \hbar \omega_{\mathbf{k}} + \sum \frac{k_B T}{2} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_{\mathbf{k}}}{k_B T} \right) \right]
\]
and obtained the following result, which can be used in calculations of the elastic constants at finite temperatures:

\[
\frac{1}{V} \frac{\partial^2 F}{\partial \eta_i \partial \eta_j} = \frac{1}{V} \left( \frac{\partial^2 F_{\eta \eta}}{\partial \eta_i \partial \eta_j} \right) + \frac{1}{V} \sum_{i,k} \left[ \gamma_{ik}^{\eta_i} \gamma_{ik}^{\eta_j} \right] \left( F_{\eta \eta,ik} - \gamma_{ik}^{\eta_i} \gamma_{ik}^{\eta_j} C_{V\eta,ik} T \right) \]

[141]

2.06.2.2.4 Elastic anisotropy in the Earth’s interior

While most of the lower mantle and the entire outer core are elastically isotropic, seismological studies have indicated seismic anisotropy amounting to a few percent in the upper mantle, lowermost mantle (D* layer), and in the inner core. This anisotropy can be due to lattice-preferred orientation (e.g., appearing due to plastic flow orienting crystallites in a rock), or due to their reasons such as shape-preferred orientation or macroscopic-scale ordered arrangements of crystals of different minerals and/or molten rock. The most directly testable case is lattice-preferred orientation. Elastic anisotropy causes splitting of seismic waves – much akin to birefringence of light waves in anisotropic crystals. For an overview, see Anderson (1989).

One would expect that crystals will orient their easiest plastic slip planes parallel to the direction of the plastic flow (e.g., in convective streams). The selection of a single dominant slip plane is, of course, a simplification – which, however, leads to a most useful model of a transversely isotropic aggregate (where crystallites have parallel slip planes, but within the slip plane their orientations are random). For the case of a transversely isotropic aggregate with a small degree of anisotropy, Montagner and Nataf (1986) considered the following parameters (the unique axis of the transversely isotropic aggregates is set to be c-axis):

\[
\begin{align*}
A &= \frac{3}{8} (C_{11} + C_{22}) + \frac{1}{4} C_{12} + \frac{1}{2} C_{66} \\
C &= C_{33} \\
F &= \frac{1}{2} (C_{13} + C_{23}) \\
L &= \frac{1}{2} (C_{44} + C_{55}) \\
N &= \frac{1}{8} (C_{11} + C_{22}) - \frac{1}{4} C_{12} + \frac{1}{2} C_{66} 
\end{align*}
\]

[142]

From these, they derived the velocities of the shear vertically (\(v_{SV}\)) and horizontally (\(v_{SH}\)), and compressional vertically (\(v_{PV}\)) and horizontally (\(v_{PH}\)) polarized waves:

\[
\begin{align*}
v_{PV} &= \sqrt{\frac{A}{\rho}} \\
v_{SH} &= \sqrt{\frac{N}{\rho}} \\
v_{SV} &= \sqrt{\frac{S_{\perp}}{\rho}} \\
v_{PH} &= \sqrt{\frac{L}{\rho}} 
\end{align*}
\]

[143]

What determines the dominant slip system? Strictly speaking, the dislocations – their number and the activation energy for their migration – should be the smallest for the best slip system. However, on the example of h.c.p.-metals, Legrand (1984) has demonstrated that a simplified criterion works very well. The product of the stacking fault enthalpy \(\gamma\) calculated per area \(S_f = (\gamma = \Delta H_f / S_f)\) and the shear elastic constant relevant for the motion of this stacking fault is smallest for the preferred slip plane. For example, comparing basal \(\{0001\}\) and prismatic \(\{1010\}\) slip for h.c.p.-metals, the ratio

\[
R = \frac{\gamma_{0001} C_{44}}{\gamma_{1010} C_{66}}
\]

[144]

is greater than 1 in cases of prismatic slip and smaller than 1 for materials with basal slip. This criterion was used by Poirier and Price (1999) in their study of the anisotropy of the inner core and, in an extended form, by Oganov et al. (2005b) in their revision of the nature of seismic anisotropy of the Earth’s D* layer (see also Section 2.06.4.2).

2.06.3 Phase Transitions of Crystals

The study of phase transitions is of central importance to modern crystallography, condensed matter physics, and chemistry. Phase transitions are a major factor determining the seismic structure of the Earth and thus play a special role in geophysics (e.g., Ringwood, 1991).

2.06.3.1 Classifications of Phase Transitions

A popular classification of phase transitions was proposed by Ehrenfest in 1933 (for a historical and scientific discussion, see Jaeger (1998)), distinguishing between first-, second-, and higher-order phase transitions. For the ‘first-order’ transitions the ‘first’ derivatives of the free energy with respect to \(P\) and \(T\) (i.e., volume and entropy) are discontinuous at the transition point; for ‘second-order’ transitions the ‘second’ derivatives (compressibility, heat capacity, and thermal expansion)
are discontinuous, and so forth. In some cases, the order of the same phase transition is different at different P–T conditions: isosymmetric transitions must be first order, but become completely continuous (infinite-order) transitions at and above the critical temperature. Some transitions change under pressure/temperature from first to second order; the crossover point is called the tricritical point. Among the examples of systems with tricritical crossover are NH$_4$Cl (Garland and Weiner, 1971), zone-center cubic-tetragonal transition in BaTiO$_3$ perovskite, possibly the transition from calcite to metastable calcite (II) in CaCO$_3$ (see Hatch and Merrill (1981)) and, possibly the α–β transition in quartz (SiO$_2$). For example, the order–disorder transition in NH$_4$Cl from a phase with a complete orientational disordering of the NH$_4$-group ($Pm\overline{3}m$) to an ordered phase ($P4\overline{3}m$) is first order at 1 atm and 242 K, but becomes second order at the tricritical point, 0.15 GPa and 256 K. Therefore, the order of the transition is not something fundamentally inherent to the transition.

The first structural classification was due to Buerger (1961), who distinguished two main types of phase transitions — those with and without changes of the first coordination number, respectively. Each of these types was further classified into reconstructive (i.e., requiring formation/breaking of bonds), displacive, order–disorder, electronic, etc., transitions.

Even though Buerger’s classification is purely structural, it naturally gives some insight into thermodynamics and kinetics of phase transitions. For instance, reconstructive transitions are first order and require activation (and, hence, are kinetically controlled) (Polymorphs of carbon (graphite, diamond) and Al$_2$SiO$_3$ (minerals kyanite, andalusite, and sillimanite, see Kerrick (1990)) are classical examples. All the transitions between these minerals are first-order reconstructive and require substantial activation energies to proceed; therefore, all the three minerals can coexist at not very high temperatures for millions of years in nature.) Also, as recognized by L. D. Landau in 1937 (see Landau and Lifshitz, 1980), for a second-order transition the two phases must be structurally related, and their symmetry groups must conform to certain group–subgroup relations.

### 2.06.3.2 First-Order Phase Transitions

Thermodynamics of first-order transitions are based on the Clausius–Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$  \[[145]\]

where $\Delta S$ and $\Delta V$ are the entropy and volume differences, respectively, between the phases. Using [145] one can calculate the slopes of the equilibrium lines of phase coexistence. This relation is valid only for first-order transitions, because for second-order transitions both $\Delta V$ and $\Delta S$ are equal to zero. The transition temperatures and pressures can be found from accurate atomistic or quantum-mechanical total energy calculations (e.g., Alfè et al., 1999; Oganov et al., 2003, 2005a; Oganov and Ono, 2004, 2005; Umemoto et al., 2006). Only when the two phases are structurally similar can one apply approximate analytical theories, such as Landau theory (which was initially devised to study second-order phase transitions).

A relation, analogous to [145], for second-order transitions was derived by Ehrenfest:

$$\frac{dP}{dT} = \frac{\Delta C_p}{\Delta T \Delta \alpha}$$  \[[146]\]

where $\Delta C_p$ and $\Delta \alpha$ are the jumps of the heat capacity and thermal expansion at the transition. However, precise experiments, computer simulations, and accurate theories indicate a qualitatively different behavior of the heat capacity — instead of having a finite jump, it logarithmically diverges to infinity on both sides of the transition. This ‘λ-behavior’ invalidates the Ehrenfest relation.

### 2.06.3.3 Landau Theory of First- and Second-Order Transitions

When the structural changes occurring upon transition are small, it is usually possible to define an order parameter (or several order parameters), whose continuous change describes all the intermediate structures on the transition pathway. The simplest expression for the free energy is the Landau potential

$$G(Q) = G_0 + \frac{1}{2} A(T-T_c)Q^2 + \frac{1}{3} BQ^3 + \frac{1}{4} CQ^4 + \cdots$$  \[[147]\]

where $T_c$ is the critical temperature, and $G_0$ the free energy of the phase with $Q=0$ (e.g., high-temperature high-symmetry disordered phase). Landau’s assumption that the second term of [147] is simply proportional to $(T-T_c)$ was analyzed and justified mathematically by Sposito (1974). The entropy as a function of the order parameter is simply
\[ S(Q) = -\frac{\partial G(Q)}{\partial T} = S_0 - (1/2)AQ^2. \]

This dependence of the entropy on the order parameter is most appropriate for displacive phase transitions. (For order–disorder transitions, the entropy is more accurately expressed as

\[ S(Q) = S_0 - R[(1 + Q)\ln(1 + Q) + (1 - Q)\ln(1 - Q)]. \]

The internal energy is then

\[ E(Q) = E_0 - (1/2)AT_C Q^2 + (1/3)BQ^3 + (1/4)CQ^4 + \cdots. \]

In the case \( A > 0, B > 0, C > 0 \), this corresponds to a double-well potential \( E(Q) \). (More than two minima can exist for higher-order polynomials [147].) For second-order transitions the odd-order terms in [147] must be zero, making the double well symmetric. (This is only one of the necessary conditions. Other necessary conditions were formulated by Birman (1966) using group theory.)

Consider a second-order transition

\[ G(Q) = G_0 + \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{4}CQ^4 + \cdots \quad [148] \]

One can observe that at the transition point \( T = T_C, Q = 0 \) the second derivative of \( F \) with respect to \( Q \) changes sign, corresponding to freezing in of a soft mode below \( T_C \) and a corresponding structural distortion. For first-order transitions, complete mode softening does not occur at \( T = T_C \).

Second-order phase transitions are always characterized by group–subgroup relations: the symmetry group of one (‘ordered’, usually low-temperature) phase is a subgroup of the symmetry group of the other (‘disordered’, usually high-temperature) phase. The two symmetrically equivalent minima then correspond to the same ordered phase, and can be considered as ‘twin domains’, related by a symmetry element present in the disordered phase, but absent in the ordered one (Figure 8).

The potential [147] is often complicated by the coupling of the order parameter to lattice strains. In such cases, the potential will be

\[ G(Q) = \left( G_0 + \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + \cdots \right) + a_1Q\epsilon + a_2Q^2\epsilon^2 + a_1Q^2\epsilon + \frac{1}{2}C\epsilon^2 + \cdots \quad [149] \]

where \( a_1, a_2, a_3 \) are coupling coefficients, and \( C \) is an elastic constant. Coupling of the order parameter to strains can cause a first-order behavior even for a symmetric \( E(Q) \).

In some cases, more than one order parameter is required to describe a phase transition. Then, for the case of two order parameters, the Landau potential looks like

\[ G(Q) = G(Q_1) + G(Q_2) + \xi_1Q_1Q_2 + \xi_2Q_1^2Q_2 + \xi_3Q_1Q_2^2 + \cdots \quad [150] \]

where \( \xi_1, \xi_2, \) and \( \xi_3 \) are coupling coefficients for the \( Q_1, Q_2 \) coupling. In cases where odd-order terms of the kind \( \xi Q_1Q_2Q_3 \) are present, the transition must be first order. For a detailed general account of Landau theory, see Landau and Lifshitz (1980), Carpenter and Salje (1998, 2000).
theory assumes that all the neighboring unit cells have the same configuration; therefore, domain structures and fluctuations of the order parameter in space and time are not treated. This problem becomes severe in the vicinity of $T_C$ (in the so-called Ginzburg interval). For second-order transitions Landau theory predicts $Q \sim (T_C - T)^{1/2}$, while experiments indicate $Q \sim (T_C - T)^{1/4}$. The critical exponent of 1/3 has been confirmed many times by numerical computer simulations and could be explained only with the advent of renormalization group theory. (In fact, experiments give mean-field critical exponents far from $T_C$ but nearer $T_C$ there is a crossover from the mean-field to critical behavior, where the critical exponents depart significantly from mean-field predictions.) Landau theory cannot explain the logarithmic divergence of the heat capacity near the critical point — instead, it yields a finite jump. Finally, Landau theory does not consider quantum effects at low temperatures. As a consequence, it does not reproduce experimentally observed order parameter saturation at low temperatures; instead, it predicts a steady increase of the order parameter with decreasing temperature.

### 2.06.3.5 Ginzburg–Landau Theory

In 1950, V. L. Ginzburg and L. D. Landau (see Landau and Lifshitz (1980) and Bowley and Sánchez (1999)) considered the case of an order parameter slowly varying in space. This leads to the simplest theory beyond the mean-field approximation, where the free energy becomes a ‘functional’ of the order parameter, and an additional term proportional to the square of the gradient of the order parameter appears:

$$F[Q(r)] = \int \left\{ f(Q) + Q \frac{\lambda}{2} |\nabla Q|^2 \right\} dr \quad [151]$$

with the stiffness parameter $\lambda > 0$. For example, for a second-order transition

$$F[Q(r)] = \int \left\{ \frac{1}{2} a(T - T_C) Q^2(r) + \frac{1}{4} k Q^4(r) + \frac{1}{2} \lambda |\nabla Q|^2 \right\} dr \quad [152]$$

The order parameter is then expressed as a sum of a constant term (the average order parameter) and fluctuations, given by a Fourier series:

$$Q(r) = Q_0 + \sum_k Q_k e^{ik} \quad [153]$$

Equation [152] can be rewritten as

$$F[Q(r)] = \int \left\{ f(Q) + Q \frac{\lambda}{2} |\nabla Q|^2 \right\} dr \quad [154]$$

Let us consider the case $f'' < 0$. In this case, the system is unstable against all fluctuations whose wave vectors satisfy $f'' + \lambda k^2 > 0$. Hence, the maximum unstable wave vector is $k_c = \sqrt{f''}/\lambda$. The correlation length $\xi$ is

$$\xi = k_c^{-1} = \sqrt{\frac{\lambda}{f''}} \quad [155]$$

Ginzburg and Landau have proposed a criterion of the validity of Landau theory, defining the following value:

$$r(T) = \frac{f_m \xi}{k_B T} \quad [156]$$

where $f_m$ is the difference of energies at the energy maximum and minimum. If $r(T) > 1$, fluctuations are not important, and Landau theory is valid. When $r(T) < 1$, fluctuations are essential and Landau theory is invalid; this occurs in the vicinity of $T_C$ (in the temperature region called Ginzburg interval). Ginzburg intervals are usually quite narrow (of the order of $\sim 10 \text{ K}$).

For second-order transitions, $f_m = a^2(T - T_C)/4b$ and

$$\xi = \frac{\sqrt{\frac{\lambda}{2a(T_C - T)}}}{k_B T} \quad [157]$$

Ginzburg–Landau theory is still approximate and does not reproduce experimental critical exponents. Renormalization group theory overcomes all these difficulties and serves as the modern basis of theory of critical phenomena; it goes beyond the mean-field approximation and fully treats all possible fluctuations of the order parameter. Introductory texts on this theory can be found in Chandler (1987), Rao and Wilson (1983); the latter reference is the Nobel lecture of Kenneth Wilson, one of its main inventors. This theory has led to the prediction of new physical phenomena, for example, continuous lattice melting, experimentally found in Na$_2$CO$_3$ (Harris and Dove, 1995).
2.06.3.6 Ising Spin Model

This model is widely used to describe magnetic and atomic ordering processes in materials. In this model, a spin $+1$ or $-1$ is associated with each lattice site, depending on whether the magnetic moment on the site is ‘up’ or ‘down’, or whether the atom occupying the site is of the type ‘A’ or ‘B’.

The total energy of the system is

$$U = U_0 - J \sum_{i,j} S_i S_j - H \sum_i S_i$$  \[158\]

where $U_0$ is the reference energy, and $J$ the interaction parameter between the sites; if $J < 0$, unlike spins prefer to group together, and there is a tendency to ordering at low temperatures; if $J > 0$, unmixing will occur at low temperatures. Complete disorder, although unfavorable energetically, will be stabilized by the entropy at high temperatures. An external field $H$ leads to a preferred orientation of the spins. The Ising model can be analytically solved only in one and two dimensions; for three dimensions it is solved numerically, usually by the Monte Carlo method. One-dimensional Ising model exhibits no phase transitions, and at all temperatures above 0 K yields the disordered state.

Ising-like models provide an interesting route for theoretical studies of polytypism and polysomatism (see, e.g., Price (1983), Price and Yeomans (1984) and references therein). The crucial observation is the mathematical similarity between polytypic sequences (e.g., Figure 9) and one-dimensional Ising models.

The Ising model is also very attractive for studies of ordering processes; for a review the reader is referred to Warren et al. (2001), and can be generalized for the case of more than two spins (see Yeomans, 1992) – such variants will be applicable to ordering in multicomponent solid solutions and polytypic (polysomatic) systems with more than two types of layers.

The conventional Ising models assume that spins can be only ‘up’ or ‘down’, and therefore these models cannot be applied to noncollinear magnetic materials. For these cases, various Heisenberg models are appropriate, which take into account the orientations of the spins. The simplest of these models is based on the following Hamiltonian:

$$U = U_0 - J \sum_{i,j} S_i S_j - H \sum_i S_i^z$$  \[159\]

involving spin vectors $S_i$ and $S_j$. By analogy with the one-dimensional Ising model, the Heisenberg model

![Figure 9](image_url)
has no phase transitions for one- and two-dimensional systems.

2.06.3.7 Mean-Field Treatment of Order–Disorder Phenomena

The Bragg–Williams model is the simplest mean-field approach applicable to ordering phenomena. The free energy of the alloy as a function of temperature and order parameter is

\[
G = G_0 - \frac{Nz}{4} J Q^2 + Nk_B T [(1+Q) \ln(1+Q) + (1-Q) \ln(1-Q)]
\]

where \(G_0\) is the free energy of the fully disordered state, \(N\) is the number of sites where disordering occurs, the order parameter \(Q = X_{A,\alpha} - X_{A,\beta} = X_{B,\beta} - X_{B,\alpha} = 2X_{A,\alpha} - 1\), and the exchange energy \(J = E_{AA} + E_{BB} - 2E_{AB}\).

The expression [160] is analogous to the Landau potential [148] and yields the same critical exponents. In three dimensions, this model gives qualitatively reasonable results; however, even with accurate exchange energies \(J\), the predicted transition temperatures are usually a few times higher than the experimental ones (Redfern, 2000).

Drawbacks of the Bragg–Williams model can be corrected by explicitly considering short-range order. In the Bethe model (see Rao and Rao (1978)), apart from the long-range order parameter \(Q\), one or more short-range order parameters are considered. These additional parameters describe the distribution of neighbors of both kinds in the nearest proximity of each atom. The resulting critical exponents and transition temperatures are much more realistic than mean-field predictions.

In the following, we discuss features of different types of phase transitions, classified by their symmetry. This gives a new viewpoint on the variety of phenomena associated with phase transitions in solids.

2.06.3.8 Isosymmetric Transitions

Using Landau theory, it is easy to show that isosymmetric transitions must be first order, but can disappear (i.e., become fully continuous, infinite-order transitions) above the critical temperature (Bruce and Cowley, 1981; Christy, 1995). There is a complete analogy here with the liquid–gas and liquid–liquid transitions (which are also isosymmetric). All liquid, gaseous, and conventional amorphous phases are isosymmetric, having spherical point-group symmetry. At supercritical temperatures there are generally rapid, but continuous changes in all properties along any \(P–T\) path going above the critical point (Angel, 1996).

Increasingly, many crystals are now known to exhibit isosymmetric phase transitions (i.e., those for which both phases have the same space group with the same number of atoms in the unit cell, with atoms occupying the same Wyckoff positions). Such transitions can be electronic (where the electronic structure changes, e.g., Ce and SmS), structural (where the coordination or ordering of the atomic species change discontinuously, e.g., KTiOPO\(_4\)), or intermediate (both electronic and structural changes are involved, e.g., Na\(_3\)MnF\(_6\)). Metallic Ce undergoes an isosymmetric phase transition Ce(I)–Ce(IV) (see Liu and Bassett (1986) and references therein), presumably due to 6s–4f (or 5d) electronic transition. Both Ce(I) and Ce(IV) have the f.c.c. structure (space group \(Fm\overline{3}m\)). The volume change at the transition is very large (13%) at room temperature, but it rapidly decreases along the Ce(I)–Ce(IV) equilibrium line until it disappears at the critical point (2.15 GPa and 613 K). Another famous example of an electronic transition is SmS, which transforms from the low-pressure insulating phase to the high-pressure metallic phase; both phases have an NaCl-type structure. Figure 10 explains this transition.
Structural isosymmetric transitions do not involve any drastic changes in the electronic structure, but are purely atomistic. KTiOPO₄ (KTP) is known to undergo a phase transition at 5.8 GPa with a volume decrease of 2.7% with preservation of space group \( Pna2_1 \) (Allan and Nelmes, 1996). Large cages, occupied by K, lose 12% of their volume upon transition. KNO₂ (Allan and Nelmes, 1996). Large cages, occupied by K, lose 12% of their volume upon transition. 11.5%, does not alter the space group (\( Pnma \)) (Adams et al., 1988), while for potassium atoms the coordination number changes from 9 to 11. An isosymmetric (space group \( Pnma \)) phase change has been observed at 9.8 GPa for PbF₂ (Haines et al., 1998) and involves a change of the coordination number of Pb atoms from 9 to 10. \( Na_3MnF_6 \) (space group \( P2_1/m \)) is an example of a phase transition with a simultaneous change in the atomic and electronic structure. At 2.2 GPa this compound undergoes a first-order isosymmetric phase transformation, which is associated with a change of orientation of the Jahn–Teller elongation of MnF₆ octahedra (Carlson et al., 1998).

### 2.06.3.9 Transitions with Group–Subgroup Relations

There are several possibilities here, stemming from different types of subgroups/supergroups of crystal symmetry. Examples are \( \alpha \rightarrow \beta \) quartz, \( P2_1/c \rightarrow C2/c \) pyroxenes (see very interesting papers by Arlt and Angel (2000) and Arlt et al. (1998)), and \( Phm \rightarrow Pn3m \) transitions in perovskites. The second type of transitions with group–subgroup transitions involve indirect symmetry relations between two phases via an intermediate archetypal phase of a higher symmetry, which is a supergroup for symmetries of both phases. An example is BaTiO₃, where the transition between the rhombohedral and tetragonal phases can be described with reference to the higher-symmetry cubic phase. Such transitions are usually weakly first order.

The third possibility involved a transition state of lower symmetry, which is a common subgroup of the symmetries of both phases. These transitions are usually strongly first order; often they can be described as reconstructive (see Christy (1993)). The f.c.c.→b.c.c. transition in Fe can be described with reference to lower-symmetry tetragonal or rhombohedral configurations, whose symmetries are common subgroups of both symmetry groups of the b.c.c. and f.c.c. phases.

### 2.06.3.10 Pressure-Induced Amorphization

This phenomenon, discovered in 1984 in experiments on compression of ice (Mishima et al., 1984) to 1 GPa at 77 K, is still poorly understood. For detailed reviews, see excellent papers (Sharma and Sikka, 1996; Richet and Gillet, 1997).

A great number of crystals undergoing pressure-induced amorphization are known (e.g., Quartz SiO₂, coesite SiO₂, bertrandite AlPO₄, GeO₂, zeolites scolecite \( Ca_8Al_{16}Si_{24}O_{80}^{**}24H₂O \) and mesolite \( Na_{16}Ca_{16}Al_{88}Si_{24}O_{240}^{**}64H₂O \), anorthite \( CaAl_{2}Si_{2}O_{8} \), wollastonite \( CaSiO₃ \), enstatite \( MgSiO₃ \), muscovite \( KA_{13}Si_{2}O_{10}(OH)_{2} \), serpentine \( Mg₃Si₂O₅(OH)₃ \), portlandite \( Ca(OH)₂ \), as well as a few substances undergoing pressure-release amorphization, whereby high-pressure phases, when decompressed to pressures well below their stability fields, become dynamically unstable and amorphize. (This happens to the perovskite-type modification of \( CaSiO₃ \), one of the main minerals of the Earth’s lower mantle, which at ambient conditions turns to a glass within a few hours.)

Pressure-induced amorphization is always a metastable first-order transition. It occurs in the limit of dynamical stability of the crystal. Behavior of pressure-induced amorphous phases on decompression can be very different some compounds (e.g., \( Ca(OH)₂ \)) recrystallize, others (e.g., SiO₂, ice) remain amorphous. Elastic anisotropy was found in pressure-amorphized quartz by Brillouin spectroscopy (McNeil and Grimsditch, 1991) and molecular dynamics simulations (Tse and Klug, 1993). The latter study found no structural relationships between pressure-amorphized quartz and silica glass.

The mechanisms driving pressure-induced amorphization are still not quite clear. The necessary conditions are (1) higher density of the amorphous phase relative to the crystal and (2) presence of soft modes in the crystalline phase. Softening of a vibrational mode at a single point of the Brillouin zone should drive a transition to a crystalline (if the soft wave vector is rational) or incommensurate (if the wave vector is irrational) phase. Simultaneous or nearly simultaneous softening of a phonon branch at a range of \( k \)-vectors could produce an amorphous phase (Keskar et al., 1994; Binggeli et al., 1994; Hemmati et al., 1995). Any atomic displacement, expressible as a combination of soft modes, lowers the energy; the multitude of possible combinations gives rise to the disorder. However, a large degree of order should remain because the displacements are expected to be small and because only displacements
related to the softening phonon branch are allowed to freeze in. Simultaneous softening of a phonon branch along a direction in the Brillouin zone implies weak dispersion of this branch, which is most naturally achieved when the unit cell is large. Indeed, crystals with complicated open structures and large unit cells are more prone to pressure-induced amorphization.

2.06.4 A Few Examples of the Discussed Concepts

Very briefly, we will discuss some recent results illustrating the use of the notions and theories discussed above. These include the calculation of the temperature profile of the Earth’s lower mantle and core, polytypism of MgSiO$_3$ post-perovskite and seismic anisotropy of the Earth’s D’ layer, and spin transition in (Mg, Fe)O magnesiowüstite.

2.06.4.1 Temperature Profile of the Earth’s Lower Mantle and Core

Equation [26] can be rewritten, taking into account eqn [85b], as follows:

$$
\frac{\partial \ln T}{\partial \rho} = \gamma_a
$$

This formula describes adiabatic change of temperature upon compression and is relevant for first-order estimates of the average temperature distribution in convecting mantle (where superadiabatic effects might be non-negligible) and outer core (which is very closely adiabatic). Ab initio calculations of Alfè et al. (2002) produced an estimate of the temperature at the inner–outer core boundary (5150 km depth) of 5600 K. This was calculated from the melting curve of iron, taking into account the effect of impurities (Si, S, O). While within the solid inner core the temperature is likely to be constant, the temperature distribution in the liquid and rapidly convecting outer core is adiabatic [161]. With their estimates of the Grüneisen parameter of liquid iron at relevant pressures and temperatures, Alfè et al. (2002) calculated the temperature distribution in the outer core. In particular, the core temperature at the boundary with the mantle was estimated to be in the range 4000–4300 K.

Phase-equilibrium experiments of Ito and Katsura (1989) produced another ‘anchor’ point for the calculation of the geotherm – 1873 K at the depth of 670 km (top of the lower mantle). Taking into account the Grüneisen parameters of MgSiO$_3$ perovskite and MgO periclase obtained in their ab initio simulations. Oganov et al. (2002) have calculated the adiabatic geotherm of the lower mantle. The resulting mantle temperature at the boundary with the core (2891 km depth) is 2700 K, indicating a strong thermal boundary layer with large temperature variations at the bottom of the mantle. Lateral temperature variations in the lower mantle have been estimated (Oganov et al., 2001a) by combining seismic tomography images and computed elastic constants of MgSiO$_3$ perovskite as a function of pressure and temperature (Oganov et al., 2001a). These variations were found to increase from 800 K at the depth of 1000 km to ~2000 K close to the bottom of the lower mantle.

2.06.4.2 Polytypism of MgSiO$_3$

Post-Perovskite and Anisotropy of the Earth’s D’ layer

The original findings of the post-perovskite phase of MgSiO$_3$ (Murakami et al., 2004; Oganov and Ono, 2004) came as a big surprise. The unusual crystal structure of post-perovskite and its elastic properties naturally explained most of the anomalies of the D’ layer – the D’ discontinuity and its variable depth, the anticorrelation of shear and bulk sound velocities and seismic anisotropy of the D’ layer (see Oganov and Ono (2004), Murakami et al. (2004), and Oganov et al. (2005b)).

Recently, Oganov et al. (2005b) found that MgSiO$_3$ perovskite and post-perovskite can be considered as end members of an infinite polytypic series (Figure 11) – this is a case of nontraditional polytypism (for another illustration, see Figure 9), since the ‘layers’, whose shifting produces all the structures in the polytypic series, are not weakly bound and are not even immediately obvious in the structure. All these structures are energetically very similar, and since intermediate structures have only marginally higher enthalpies than perovskite or post-perovskite, these phases could be stabilized by temperature and/or impurities in the Earth’s lowermost mantle. This polytypism with low-energy stacking faults has interesting implications for plasticity of MgSiO$_3$ post-perovskite and for seismic anisotropy of the D’ layer.

Initially, {010} slip planes parallel to the silicate sheets of the post-perovskite structure were expected
to be dominant in post-perovskite. However, \textit{ab initio} simulations (Oganov \textit{et al.}, 2005b) found that the \{110\} slip planes are much more favorable. In particular, this conclusion was supported by applying Legrand’s criterion – generalization of eqn [144]. With these slip planes and using the method of Montagner and Nataf (1986), eqns [142] and [143], one obtains a more consistent interpretation of seismic anisotropy of the D\textsuperscript{0} layer than with the \{010\} slip planes. In particular, much smaller degrees of lattice-preferred orientation are needed to explain the observed seismic anisotropy and there is now a possibility to explain the observed (Garnero \textit{et al.}, 2004; Wookey \textit{et al.}, 2005) inclined character of anisotropy. Subsequent radial diffraction experiments on analog MgGeO\textsubscript{3} post-perovskite (Merkel, personal communication) have confirmed the prediction of Oganov \textit{et al.} (2005b) on the dominant role of the \{110\} slip planes in MgSiO\textsubscript{3} post-perovskite. Furthermore, recent seismological studies (Wookey, personal communication) found that only \{110\} slip is consistent with observations.

\subsection{Spin Transition in (Mg, Fe)O Magnesiowüstite}

Iron impurities play a large role in determining the properties of Earth-forming minerals. One particular complication arising from the presence of these impurities is the possible pressure-induced transition of Fe\textsuperscript{2+} (or Fe\textsuperscript{3+}) impurities from the high-spin into the low-spin state. Typically, crystal fields induced by the O\textsuperscript{2–} ions at low pressures are weak, and transition metal ions prefer to adopt the high-spin configurations (like in free ions). However, under pressure the increasing crystal field and the additional \textit{PV} term in the free energy prompt these ions to adopt much more compact low-spin forms (it is well documented that ionic radii are much larger for high-spin ions than for low-spin ones – for example, Shannon and Prewitt (1969). Recent studies of such a transition in (Mg, Fe)O magnesiowüstite (Badro \textit{et al.}, 2003; Lin \textit{et al.}, 2005) demonstrated that this transition might have large effects on physical properties of minerals.
This spin transition is isosymmetric, and as such it must (see Section 2.06.3) be first-order at low temperatures and fully continuous above some critical temperature $T_{cr}$. While at 0 K the low-pressure phase will contain only high-spin Fe$^{3+}$ ions, and only low-spin ions will be present in the high-pressure phase, on increasing temperature there will be an increased degree of coexistence of the two spin states in the same phase – as a consequence, the first-order character of the transition decreases with temperature. At $T_{cr}$ the miscibility of high- and low-spin ions become complete and the transition becomes fully continuous (infinite order, rather than first or second order); $T_{cr}$ is proportional to the enthalpy that arises from the deformation of the structure due to insertion of a ‘wrong’-spin ion. While quantitative aspects of this transition are actively studied by several groups, the most important qualitative features (in addition to those mentioned above) are immediately clear:

1. Large positive Clapeyron slope (since at high temperatures magnetic entropy is large for high-spin Fe$^{3+}$ and zero for low-spin Fe$^{3+}$).
2. Low $T_{cr}$, perhaps several hundred kelvin, since for relevant compositions (e.g. Mg$_{0.8}$Fe$_{0.2}$O) the energetic effects of Fe incorporation and the enthalpy of ‘spin mixing’ will be rather small.

At lower-mantle temperatures the transition is likely to be continuous. A schematic phase diagram is shown in Figure 12. Simplified theory of the spin transition in (Mg, Fe)O was developed by Sturhahn et al. (2005).

**Figure 12** Schematic phase diagram for a system with a spin transition, for example, (Mg,Fe)O. Thick solid line indicates first-order transition, and thick dashed line indicates continuous transition. Gray lines show the degree of spin miscibility (numbers: concentration of low-spin species relative to the total number of iron atoms). Above $T_{cr}$ the transition is fully continuous.

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