7
Structure and Properties

7.1
The Interpretation of Properties from Model Calculations, Correlations Between Properties

Among the most important tasks of material sciences today, aside from the experimental characterization via structural determination and the measurement of physical properties is, in particular, the interpretation and prediction of crystal properties from the chemical constituents, a field residing in the domain of crystal chemistry. In this section we present a brief overview on the current situation.

The first step is the determination of the structure, i.e., the atomic arrangement of the lattice particles which we denote by the motif and metric of the lattice. The furthermost goal, namely, with the help of *ab-initio* calculations based on quantum theoretical and thermodynamic considerations to make assured statements on possible stable crystal structures was successfully realized for a few simple chemical constituents only in the last years. This was due not only to the immense increase in computational power of the computer systems but also to the further development of mathematical tools such as the Hartree–Fock theory or density functional methods (see, for example, Winkler, 1999). Although, in principle there seems to be no insurmountable barriers in the prediction of structures of complex substances, one may not anticipate that all problems of structure formation will be satisfactorily solved in the near future. This applies, in particular, to substances containing large structural units of low inherent stability, for example, large organic molecules or complex adducts of inorganic and organic groups of substances.

The same applies to the second step of the prediction, namely the determination of chemical and physical properties of arbitrary substances of known crystal structure (including chemical constituents). This has only been achieved to a satisfactory degree for a fraction far under one per mill of the approximately 0.5 million structurally known substances to date (listed in the crystal structure data bank ICSD and CSD). Since the experimental evaluation

of most of the crystal-physical properties discussed in this book are still considerably time consuming, in particular, even the manufacture of sufficiently large single crystals of high quality (low density of imperfections), the automatic determination of the properties remains an urgent goal should a rich collection of data be made available not only for a broad crystal-chemical interpretation but also for the selection of application specific materials. And, because the precision of the experimental data is often far higher than that achieved through calculation, one will not be able to abandon the experimental method at the present stage, i.e., for the time being, one cannot do away with single crystal growth and practical crystal physics in many areas of work. This is especially true, for example, for the determination of the temperature dependence of the properties.

If one is content with a few quantitative or only qualitative predictions, then one can fall back on the models already developed at the beginning of the last century. The largest advance at that time was provided by the Born lattice theory (see, for example Geiger–Scheel: Handbuch der Physik XXIV, 1933, and Born & Huang 1954). This theory allowed the approximate calculation of a series of properties from simple models of the interaction between lattice particles. The attractive forces, in particular, the Coulomb interaction in ionic crystals and the dipole–dipole or multipole–multipole interactions in the so-called molecular crystals are in equilibrium with the repulsive forces of the negatively charged electron shells. The latter also result from Coulomb interactions as well as from Pauli's exclusion principle. One of the simplest statements for the interaction potential of two ions is represented by the sum $\Phi_{ij} = Kq_iq_j/r_{ij} + b/r_{ij}^n - c/r_{ij}^6$. The first term is the Coulomb potential. K is the constant of the given system of measurement, q_i and q_j are the charges of the ith and jth point-shaped ions and r_{ij} is the distance between the ions. The second term takes into account the repulsion, whereby the exponent n, for example, in alkali halides takes on a value between 10 and 12. Finally, the multipole–multipole interactions are approximated by the third term, the van der Waals term. These quantities fix the given interaction. The summation over all ion pairs ij of the crystal then yields the lattice energy. This is equivalent to the energy released when the ionized, however, not isolated particles come together to form the lattice from a virtual infinite distance. This procedure is also suitable for the calculation of simple properties in types of cubic crystals such as the alkali halides.

In even simpler models one assigns point masses to the particles coupled via springs (spring model, harmonic approximation). The unique advantage of these models lies in their direct visual quality in contrast to the complex operations of *ab-initio* calculations. That is, correlations are more likely to be recognized and qualitatively understood.

The effects of particle thermal motion are first considered in a second step by allocating the spring constants a certain dependence on the amplitude of the vibrations. In this manner the so-called anharmonic effects, for example, thermal expansion and the temperature and pressure dependence of many properties can be calculated. Since, except for symmetry properties, the description of the interaction, at least in simple crystals, requires very little data, namely only atomic distance and the spring constant associated with the respective binding, the different types of properties calculated with this method must exhibit close correlation to these parameters and among themselves. In particular, a strong correlation is expected to the elastic properties because of their direct coupling to the spring constants thus playing a key role in these types of considerations. In Table 7.1 we present an overview of some important relationships, which we, however, are unable to discuss here in any detail. Corresponding correlations must also exist with respect to the anisotropy of the properties. Table 7.2 lists some interesting examples.

Deviations from such correlations always provide an indication of special structural details and binding properties not taken into consideration in simple models. But just because of this, the models can be improved by the addition of further criteria.

For a crude review of the relationship between structure and properties we make a broad division of the properties into two groups which, however, is not always unequivocal:

1. Additive or quasiadditive properties,

2. Nonadditive properties.

7.1.1
Quasiadditive Properties

Additivity refers to the corresponding properties of the particles (constituents: atoms, ions, molecules or particle complexes such as chains, bands, layers, polyhedric structures). That is, an additive property of the given substance should be able to be calculated from the sum of the parts of the constituent properties. Here we are mainly dealing with scalar properties, hence independent of direction and thus independent of a property of a reference system such as spacial mean values. Scalar invariants come into consideration with tensor properties as they are easy to calculate from the complete tensor. This applies especially to cubic crystals.

For our purposes we describe the chemical constituents of a substance A by the sum formula $A = (A_1)n_1(A_2)n_2 \ldots (A_q)n_q$, where each A_j stands for a certain element. Unfortunately, the sequence is not fixed in general except

Table 7.1 Correlation of physical properties and elastic properties in groups of isotypic and chemically related crytals. ↑: positively correlated with c_{ij}; ↓: negatively correlated with c_{ij}.

Property	Correlation	Explanation
$\dfrac{\text{lattice energy}}{\text{volume}} = E_0$	↑	lattice-theoretical models yield $c_{ij} \sim E_0$.
average surface energy $\bar{\sigma}$	↑	$\bar{\sigma} \sim E_0$.
melting temperature T_0	↑	melting occurs when thermal activation results in a certain losening of bonds (Lindemann formula).
impression hardness H (resistance against plastic deformation)	↑	critical flow strain $\sim$ elastical shear resistance.
abrasive strength F (yield strength)	↑	critical yield strain $\sim c_{ij}$.
Debye temperature $\Theta_D = \dfrac{h\nu_D}{k}$ h Planck constant, k Boltzmann constant, ν_D Debye frequency	↑	Debye theory yields $$\Theta_D^{-3} = \left(\frac{k}{h}\right)^3 \frac{V_0}{9} \int \sum_{i=1,2,3} \frac{1}{v_i^3(\boldsymbol{g})}\,\mathrm{d}\Omega$$ V_0 average volume of particles, $v_i(\boldsymbol{g})$ propagation velocities of waves in direction $\boldsymbol{g}$. Integration over all spatial directions is implied.
specific heat C_V at low temperatures	↓	At low temperatures, the Debye model yields $C_V = 12\pi^4 Nk/5(T/\Theta_D)^3$ für $T < \Theta_D$, N number of particles per mole.

Table 7.1 *(continued)*

Property	Correlation	Explanation
thermal conductivity λ	←	The Debye formula for thermal conductivities of dielectrics is $\lambda \sim C_V \bar{v} \bar{l}$, $\bar{v}$ average speed of sound in the respective direction, $\bar{l}$ mean free path of phonons.
thermal expansion α	→	The Grüneisen relation $\alpha = \dfrac{\gamma C_V}{3VK^{-1}}$ holds, where K is the volume compressibility. The Grüneisen constant $\gamma = -d\log\Theta_D/d\log V$ varies only slightly in isotypical series (e.g. $\gamma \approx 2$ for NaCl).
infrared limiting frequencies	←	The force constants (spring constants) of the oscillators are proportional to c_{ij}.
molar polarization and dielectricity constants of non-ferroelectric crystals, refractivities	→	The deformability of electron clouds correlates inversely with bond energy.
piezoelectric effects in polar crystals	→	Elastically more "soft" crystals suffer more pronounced deformation upon mechanical stress.
piezooptic effects	→	Elastically more "soft" crystals suffer more pronounced deformation upon mechanical stress.

Table 7.2 Examples of correlations of the anisotropic character of physical properties in strongly anisotropic crystals. As a measure of the anisotropy, the ratio of the maximum and minimum values of the respective property is given. $E = \rho \sum_{i=1,2,3} v_i^2$ dynamic elasticity, K linear compressibility under hydrostatic pressure, F abrasive strength (in xylene using corundum M35), α linear thermal expansion, λ thermal conductivity, n refractivity (at 600 nm). All values for 293 K. $\oplus$ and $\ominus$ indicate that the maximum and minimum values are observed in the direction u from the maximum of E, respectively.[*]

Crystal type	$\dfrac{E_{max}}{E_{min}}$	u	$\dfrac{K_{max}}{K_{min}}$	$\dfrac{F_{max}}{F_{min}}$	$\dfrac{\alpha_{max}}{\alpha_{min}}$	$\dfrac{\lambda_{max}}{\lambda_{min}}$	$\dfrac{n_{max}}{n_{min}}$
NaNO$_3$ ($\bar{3}$m)	1.52	[100]**	4.08$\oplus$	3.1$\oplus$	12.2$\ominus$	1.3$\oplus$	1.19$\oplus$
turmaline (3m)	1.53	[100]**	1.86$\oplus$	–$\oplus$	2.38$\oplus$	1.35$\oplus$	1.015$\oplus$
C(NH$_2$)$_3$(SO$_4$)$_2$ · 6H$_2$O (3m)	1.90	[100]**	49.6$\ominus$	1.9$\oplus$	9.2$\ominus$	3.0$\ominus$	1.06$\oplus$
rutile (TiO$_2$, 4/mm)	1.23	[001]	1.97$\ominus$	–$\oplus$	1.29$\oplus$	1.43$\oplus$	1.11$\oplus$
KH$_2$PO$_4$ ($\bar{4}$m)	1.32	[100]	1.06$\ominus$	1.5$\ominus$	1.59$\ominus$	1.3$\oplus$	1.03$\oplus$
α-KNO$_3$ (mmm)	1.56	[100]	−2.99$\oplus$	6.1$\oplus$	8.3$\ominus$	1.2$\oplus$	1.13$\oplus$
calcium formiate (mmm)	1.54	[100]	−4.7$\ominus$	1.7$\oplus$	−4.1$\ominus$	2.16$\oplus$	1.45$\oplus$
gypsum (CaSO$_4$ · 2H$_2$O, 2/m)	1.7	$\approx [\bar{1}01]$	3.64$\ominus$	8.5$\oplus$	26.5$\ominus$	2.4$\oplus$	1.005$\oplus$

[*] In monoclinic and triclinic crystals, these directions can only approximately be identical.

[**] In trigonal-hexagonal arrangement.

for organic substances. In another representation the constituents are decomposed in thermodynamically stable components B_j according to $A = (m_1 B_1) \cdot (m_2 B_2) \cdot \ldots \cdot (m_q B_q)$. Finally, it is common to designate chemical constituents according to cations and anions as well as molecular components as with the hydrated salts for instance. As an example we mention potassium alum $A = H_{24}O_{12}AlS_2K = \frac{1}{2}K_2O \cdot \frac{1}{2}Al_2O_3 \cdot 2SO_3 \cdot 12H_2O = KAl(SO_4)_2 \cdot 12H_2O$.

To calculate the mole weight M per formula unit of substance A we set $M = \sum n_j A_j$, where for A_j we write the average atomic weight of the given element. For a direct comparison of a substance A with its constituents it is often convenient to express n_j, the relative fraction of the jth type of atom of the mole weight by the mole fraction $n'_j = n_j / \sum n_j$. The modified sum formula $(A_1)n'_1(A_2)n'_2 \ldots (A_q)n'_q$ then contains L atoms ($L = 6,022 \cdot 10^{23}\mathrm{mol}^{-1}$ Avogadro's number).

Examples of the 1. group are:

(a) The average magnetic susceptibility κ of nonferromagnetic ionic crystals is $\kappa(A) \approx \sum n_j \kappa_j$ with $\kappa_j = \kappa(A_j)$ per mole.

(b) Faraday effect, expressed by the Verdet constant *Ver*. $Ver(A) \approx \sum n_j Ver_j$ with $Ver_j = Ver(A_j)$ for cubic crystals and is valid approximately for noncubic ionic crystals (Haussühl, Effgen 1988; Kaminsky, Haussühl, 1993).

(c) Mole polarization of ionic crystals. The Clausius–Mossotti formula links the average polarizability α per unit volume in the low frequency range with the average relative dielectric constant ϵ_{rel} according to $(\epsilon_{\mathrm{rel}} - 1)(\epsilon_{\mathrm{rel}} + 2) = L\rho\alpha/3\epsilon_0 M \approx \sum N_j \alpha_j / 3\epsilon_0$ (see Section 4.3.3). ρ is the density, M is the mole weight, N_j is the number of jth types of ions per unit volume and α_j is their polarizability. Then $\alpha \approx \sum n_j \alpha_j$ with $n_j = N_j M / L\rho$. α and α_j are then functions of pressure, temperature, frequency and so on.

In the range of optical frequencies ϵ_{rel} is replaced by the average refractive index $n = (n_1 + n_2 + n_3)/3$ (n_i principal refractive index). One then obtains the Lorenz–Lorenz formula $(n^2 - 1)(n^2 + 2) = L\rho R/3\epsilon_0 M \approx \sum N_j R_j / 3\epsilon_0$. R is the mole refraction and R_j is the refraction of the jth type of atom. Hence $R \approx \sum n_j R_j$. The quasiadditivity allows the summation over the R-values of the stable components of the given substance. For example, $R(Mg_2SiO4) \approx 2R(MgO) + R(SiO_2)$.

Also, the average optical activity α_{optact} can be estimated according to $\alpha_{optact} \approx \sum n_j \alpha_{optact}(A_j)$ (per mole) provided it is generated by primarily chiral particles possessing an average chirality of $\alpha_{optact}(A_j)$.

(d) Constituents with similar types of binding possess a mole volume V_{mol} that according to $V_{\text{mol}} \approx \sum m_j V_j$ with $V_j = V_{\text{mol}}(A_j)$ can be estimated from the mole volumina of the components.

(e) The lattice energy Φ in ionic crystals (per formula unit) can, according to Fersman and Kapustinsky, be estimated quasiadditive with surprising accuracy from the "energy coefficient" Φ_j of the given substance according to $\Phi \approx \sum m_j \Phi_j$ (see for example Saukow 1953). The quasiadditivity is also valid for components. For example, one obtains for the spinel $MgAl_2O_4 = MgO \cdot Al_2O_3$ the value $\Phi(MgO \cdot Al_2O_3) \approx \Phi(MgO) + \Phi(Al_2O_3)$.

(f) The X-ray mass attenuation coefficient μ^* which exhibits a hardly measurable anisotropy in the wavelength range $0.03\,\text{nm} < \lambda < 0.3\,\text{nm}$ and is thus quasiisotropic, can be calculated from the mass attenuation coefficients μ_j^* of the atomic constituents ($\mu* = \mu/\rho$; μ is the linear absorption coefficient defined by $I = I_0 e^{-\mu x}$, where I_0 is the primary intensity and I is the observed intensity after passing through a plane parallel plate of thickness x): $\mu^*(A) = \sum n_j A_j \mu_j^* / \sum n_j A_j$. The substance A is noted in the form of the sum formula. The associated atomic weights are written for A_j. The wavelength dependence of μ_j^* varies considerably under the elements. Hence, from the measurement of $\mu^*(A)$ at different wavelengths one obtains a statement on the chemical constituents of A, in particular with very small and thin probes (X-ray absorption analysis; see for example Taschentext Kristallstrukturbestimmung). Incidentally, this relationship is also quite well fulfilled for nonionic bound crystals.

(g) The volume compressibility $K = -d\log V/dp$ is expressed by $K \approx \sum m_j (V_j/V) K_j$, where V_j/V is the estimated fractional volume of the jth component of a substance and K_j is its volume compressibility. The prerequisite is that the components only show a small mutual interaction and that $V \approx \sum V_j$.

(h) The product S of the average elastic strength C and molecular volume MV, $S = C \cdot MV$, where $C = (c_{11} + c_{22} + c_{33} + c_{44} + c_{55} + c_{66} + c_{12} + c_{13} + c_{23})/9$ represents a scalar invariant of the elasticity tensor also shows a quasiadditive behavior. In ionic crystals with similar types of binding we have $S(A) \approx \sum m_j S(B_j)$, i.e., the S-values of the compound A can be calculated from the S-values of the components (Haussühl 1993). Thus one can approximately determine the average elastic strength C of a crystal type from the elastic properties of its components at known molecular volume. As an example let us consider garnet $A = Y_3Al_5O_{12}$. We expect $S(A) \approx 1,5S(Y_2O_3) + 2,5S(Al_2O_3)$. Experimentally one finds $S(A) = 4031$, $S(Y_2O_3) = 1077$ and $S(Al_2O_3) =$

1107 (S in $[10^{-20}$Nm$]$). The estimated value of $4383 \cdot 10^{-20}$Nm exceeds the expected value by about 8%. The deviations in many substances of similar types of binding lie in this order of magnitude. However, it turns out that the deviations, in part, result from a different coordination of ions. A higher coordination in the substance A compared to the average coordination of the components effects an increase of $S(A)$ compared to the average S-value of the components and vice versa. This is seen, for example, with the halides of lithium, sodium, potassium and rubidium with a NaCl type of structure (6-coordination) possessing S-values of on average about $110 \cdot 10^{-20}$Nm and the corresponding value of $123 \cdot 10^{-20}$Nm with the halides of cesium with a CsCl type of structure (8-coordination). If large deviations appear, as for example, in the high pressure modification of SiO_2 (coesite: 400; stichovite: 801) compared to α-quartz (195), then this is an indicator for a changed binding state which can also be tied to a considerable change of coordination. Hence, deviations of the additivity of the S-values can provide concrete pointers concerning structural details (Haussühl 1993).

Finally, it should be mentioned that the product of reciprocal volume compressibility and molecular volume tend to possess similar properties as the S-values.

We should not forget that persistent properties also appear in certain spectroscopic experiments. Among these are, for example, the emission and absorption lines of transitions in the deeper lying electronic shells that are little or hardly influenced in a measurable way by the binding states of the valency shells. This also applies to intramolecular excitation in the optical and infrared spectral region and can be called upon for qualitative and, in part, quantitative chemical analysis.

A special case of quasiadditivity is presented by mixed crystals with isotype components. We consider the simple case of a substance consisting of two components according to $A = (1 - x)B_1 \cdot xB_2$. To a first approximation, most properties E can be expressed by the linear relationship $E(A) = (1 - x)E(B_1) + xE(B_2)$ if x is sufficiently small (for example $x < 0.1$) and all particles of component B_2 assume the position of the corresponding particle B_1 in the crystal lattice (diadoch substitution): Vegard's rule. Naturally, this rule can be extended to mixed crystals with several isotype components. With the arbitrary substitution of particles in nondiadoch positions, which often occurs in the doping of electrically conducting substances, one observes, as expected, considerable deviations from Vegard's rule. Such properties were discussed by Smekal (1933) and designated as "structure sensitive". However, this nomenclature is no longer compatible with the concept of structure we know today.

7.1.2
Nonadditive Properties

The examples listed in Tables 7.1 and 7.2 as well as the constraints mentioned in the previous section indicate that there exists many properties closely correlated with the properties of the given component, however, not quasiadditive. We cannot discuss these individually in this book. Rather we will address those examples which on the one hand show structural features responsible for the appearance of certain properties and on the other demonstrate the existence of complicated interactions of the particles.

In the first case we think of crystals with noncentric structures. If we are dealing with tensor properties as, for example, pyroelectric, piezoelectric or nonlinear electrical and optical effects, then the associated odd-rank polar tensors must exist as argued in the respective sections. The given structures may not possess inversion centers, i.e. noncentric units of particle with preferred orientations must exist so that, in total, a structural polarity results. This can happen through stable, primary noncentric particles as, for example, the ions of CN, NO_2, BO_3, CO_3, NO_3, SO_3, ClO_3, BrO_3, IO_3, BO_4, NH_4, SiO_4, PO_4, SO_4, ClO_4, AsO_4, many amines and carbonic acids or the molecules NH_3, H_2O and alcohol. The prerequisite for the appearance of polar properties is that the polarity of the particles is not neutralized by the symmetric arrangement. The chiral stable particles make an exception. These include many amines and most amino acids whose intrinsic screw always prevents the occurrence of an inversion center unless the structure contains exactly the same number of enantiomeric particles of the same type (100% racemic mixture). This means that the chiral organic particles represent an almost inexhaustible arsenal for the directed synthesis of new crystals with polar effects.

Some crystals build a polar structure from primarily centrosymmetric atoms and ions, as, for example, low quartz α-SiO_2, silicon carbide SiC or zinc blende ZnS and their polytypes, in which the tetrahedric polarity first develops during the growth phase. There also exist numerous examples of structural chirality, resulting from the chiral arrangement of nonchiral particles (α-quartz, $NaClO_3$, $NaBrO_3$, $Na_3SbS_4 \cdot 9H_2O$).

For over twenty years many laboratories have been searching for new materials for optical data storage and data processing. This involves the application of electric or magnetic fields which result in changes to the optical properties of crystals i.e., refractive indices or absorption, which remain fixed in a metastable state for a definite time. Among these are photochromatic or holographic effects. In crystals such as lithium niobate $LiNbO_3$ or barium titanate $BaTiO_3$, doped with impurities such as iron or hydrogen, charge displacements by the electric field can generate an intense coherent light wave (laser radiation) which first vanishes after the application of heat (photo-galvanic effect). Information superimposed on the light wave in the form of ampli-

tude modulation is then stored in the crystal as a holographic lattice. The information can be retrieved and processed by suitable means so enabling the development of new and highly efficient devices for information technology. The same applies, however, with less favorable prospects, to magneto-optical storage where the light wave modulates the magnetization of thin layers of, for example, $Y_3Fe_5O_{12}$ (yttrium iron garnet) grown epitaxially on $Y_3Ga_5O_{12}$.

Many groups of substances exist in which a light wave can induce electronic transitions in the lattice particles which cause large metastable changes in optical absorption in certain temperature ranges. These changes can also be used to store the information content of the light wave. Special mention should be given to $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ and related substances, which when irradiated with blue light below 200 K trigger strong photochromatic effects coupled to a change in the electronic state of the NO group. These excited states can be quenched by increasing the temperature or also by irradiating with red light (Hauser et al. 1977,1978; Woike et al. 1993). Furthermore, it could be shown that the photochromatic properties of these groups of substances are also suitable for the generation of holographic effects thereby exhibiting the largest as yet known efficiencies (Haussühl et al. 1994; Imlau et al. 1999). The reason is that in these substances doping is not necessary, because all NO groups of the crystal are available for excitation. Apparently, these effects are not linked to a symmetry condition of the given crystal. Especially favorable is the fact that the holograms can be quickly quenched using red light just as with photochromatic effects. One disadvantage which must be still overcome is the low working temperature which, however, could be brought in the range of 300 K by varying the chemical constituents (see, for example, Schaniel et al. 2004).

A further property that can only be realized by a very special combination of the chemical composition, is superconductivity. This has been known for a long time. However, the discovery of the unexpected electrical conductivity of complicated mixed oxides with copper content by Bednorz and Müller (1986) ignited a lively and in the meantime successful search for substances with still higher transition temperatures. These efforts resulted in the achievement of a transition temperature of 125 K in $Tl_2Ba_2Ca_2Cu_3O_{10}$ a benchmark apparently not to be surpassed (Sheng, Hermann 1988). Their technological application in the generation of high magnetic fields is well under way. Apparently, not only is the participation of a certain component, namely CuO necessary, but also an unusual cooperation of several other oxides whose special participation is, however, difficult to recognize.

7.1.2.1 Thermal Expansion

We now come to discuss the the temperature and pressure dependence of the physical properties. In the concrete case we consider thermal expansion as well as elastic properties. For simply built molecular crystals as for example,

naphthalene, Kitaigorodskii (1973) was able to calculate, with the help of a potential approach that assigned characteristic parameters to the attractive and repulsive forces between two respective atoms of neighboring molecules and simultaneously took into consideration the thermal energy of the molecules, a series of properties such as lattice constants, thermal expansion, elastic constants and also thermoelastic constants in good agreement with experimental values. Other attempts, also with the alkali halides and other simply built types of crystals, to predict the more complicated properties such as thermoelastic constants have been less satisfactory.

The thermally activated motions of lattice particles of a crystal can be studied by optical methods such as Brillouin scattering (see Section 4.5.6) or in the course of crystal structure analysis. The effects of a large change in temperature influencing the lattice vibrations and excitation of certain atomic and molecular states is often made noticeable through phase transformations, changes in optical absorption (thermochromatic effects) and a few especially easily accessible macroscopic effects. Among these are thermal expansion and the temperature dependence of elastic properties. The relation derived by Grüneisen for cubic crystals $\alpha = \gamma K C_V / 3V$, where α is the linear thermal expansion coefficient, $\gamma = -d \log \Theta / d \log V$ is the Grüneisen constant with a value between 1.5 and 3, K is the volume compressibility, C_V is the specific heat per mole volume, V is the mole volume and Θ is the Debye temperature, couples at least qualitatively the thermal expansion with the specific heat and a measure for the elastic strength K^{-1}. Hence, large thermal expansions are correlated with large specific heats and small elastic strengths. For example, diamond at $300K$ possesses with its large elastic strength one of the smallest thermal expansion coefficients of about $0.87 \cdot 10^{-6} \mathrm{K}^{-1}$. In contrast, very soft organic crystals posses α values of over 100-fold higher. The temperature dependence $\alpha(T)$ close to absolute zero is determined by the T^3 law of specific heat and at very high temperatures by the quasilinear rise in compressibility with increasing temperature. Changes in the mean amplitudes of the thermal vibrations of atoms and ions as a function of temperature, determined from crystal structure analysis often agree quite well with the experimental values. In a first approximation the center of mass motion of each atomic particle is assigned a vibration ellipsoid whose semi-axis is set proportional to the amplitude of the thermal displacement vector in the respective directions of the principal axes (Debye–Waller factors; see, for example, Taschentext Kristallstrukturbestimmung). Simple isotype series such as the alkali halides or the oxides of bivalent cations of NaCl-type possess almost the same α-values. In the course of phase transformations, even second-order ones, drastic changes in thermal expansion often appear. Furthermore, it has been found that many noncubic crystals exhibit thermal expansion accompanied with considerable

anisotropic effects. From this we can infer that in general thermal expansion is hardly amenable to a quantitative structural interpretation.

7.1.2.2 Elastic Properties, Empirical Rules

From the beginnings of the lattice theory of ionic crystals, based on a Coulomb term and a term for the repulsive potential with the exponent n, hence, without the van der Waals term, one obtained the relationship $c_{ij} = F_{ij}r_{ij}^4 = Q_{ij} \cdot$mole lattice energy/mole volume. In isotype series the F_{ij}-values increase weakly with increasing mole weight due to a rise in the van der Waals potential and the exponent n of the repulsive term in heavy ions. For example, in the alkali halides of NaCl-type one observes approximately a doubling of F_{11} in passing from LiF to RbI. Also, the factors Q_{ij} do not depend on separation of the ions but are proportional to n. A similar formula exists for molecular crystals with predominantly van der Waals binding. That is, the repulsive potential determines in a very decisive way the elastic behavior. To a certain extent this statement applies qualitatively to each crystal.

A simple path for the interpretation and prediction of elastic properties is presented by the quasiadditivity of S-values already mentioned above. These allow a rough estimate of the average elastic strength from the properties of the components. A further fundamental property of the S-values consists in the fact that in isotypes and structurally or chemically closely related crystals the S-values fluctuate very little (Haussühl 1993). However, the deformation work and the stability of the electronic shells of the particles is seen to influence the S-values to a certain extent. This can be taken into account by a correction when one assigns a qualitative "hardness" to the particles which is correlated to the exponent of the repulsive term and, for example, in ions such as H^-, the electron e^- or CN^- turns out to be especially low. The experimental data compiled so far allows the formulation of a few simple insightful rules which otherwise would not be directly discernable from the complicated processes of *ab-initio* calculations.

In a next step, one can try to interpret the elastic anisotropy and the relationship to elastic shear resistances and longitudinal resistances. This must take into consideration density, strength and direction of the principal binding chains in the given structures. Directions in which many strong principal binding chains run exhibit strong elastic longitudinal effects. As examples, we mention graphite and β-succinic acid $(CH_2)_2(COOH)_2$. In graphite, strong $sp^2 - C - C$ binding chains, comparable to the sp^3-hybride bindings in diamond, lie in the plane perpendicular to the hexagonal axis, whereas along this axis far weaker interactions appear. This results in a ratio c_{11}/c_{33} of about 29, the largest known longitudinal-elastic anisotropy effect. In β-succinic acid, a monoclinic crystal of the point symmetry group 2/m, one finds the molecules along a_3 due to the H-bridges connecting the chains while in all other direc-

tions only weak van der Waals bonding occur. This results in a ratio of maximum to minimum longitudinal resistance of 12.7—the longest observed value in ionic- or molecular crystals to date.

Information concerning the ratio c_{kj}/c_{ii} of certain elastic constants can be gained from the association of the elementary cell to the Bravais lattices in which the interaction of nearest neighbors is best approximated. For example, for the cubic Bravais lattice one finds the following relationships which are easy to calculate using spring models: P-lattice: $c_{44}/c_{11} = 0$, F-lattice: $c_{44}/c_{11} = 0.5$ and I-lattice: $c_{12}/c_{11} = 1$. An instructive example is presented by the alkali halides of NaCl-type. If one goes over from LiBr or LiI with the weakest overlap of electronic shells of cations and anions to rubidium iodide with the largest corresponding overlap, then the face centered lattice of the Br^- or I^--ions must be the physically effective form of both lithium compounds, while for RbI it must be the primitive lattice formed commonly by the center of mass of the Rb and I ions. As a matter of fact one finds for c_{44}/c_{11} the values 0.49 for LiBr and 0.11 for LiI and RbI, respectively.

A further aspect is offered by the deviations from the Cauchy relations which we described by the tensor invariants $\{g_{mn}\} = \{\frac{1}{2}e_{mik}e_{njl}c_{ijkl}\}$. $\{e_{mik}\}$ is the Levi-Cività tensor (see Section 4.5.1). These deviations show a macroscopic observable effect of the atomic properties of the particles with respect to elastic behavior. Among these are asphericity, that is the deviation of the electronic shells from the spherical form, polarizability, covalence of the binding and a liquid-type interaction of the particles (Haussühl 1967). As is well known liquids possess nonmeasurable, small shear resistances in the low frequency region. Since isotropic bodies such as liquids and glasses exhibit at least the symmetry of cubic crystals, the pure shear resistances c_{66} and $(c_{11} - c_{12})/2$ corresponding to those of the cubic crystals must vanish. This means $c_{66} = 0$ and $c_{12} = c_{11}$. This gives the largest allowed deviations from the Cauchy relations, namely $g_{33} = c_{1122} - c_{1212} = c_{12} - c_{66} = c_{11}$. Particles, which because of their deformability (polarizability) contribute to conserving the volume, similar to the particles of a liquid, can be expected to show an increase in the deviations from the Cauchy relations. The same applies to strongly aspherical particles which act to magnify the transverse contraction effect, i.e., the constants $c_{ij}(i \neq j)$. In contrast, directed covalent bonding tends to increase the shear resistance, i.e., lessens the deviations from the Cauchy relations.

For practical comparison it is meaningful to refer the g_{mn} to the invariant C. The so defined quantities $\Delta_{mn} = g_{mn}/C$ are then dimensionless. As examples we consider the alkali halides, alkali cyanides, AgCl, and several oxides with cubic symmetry and the following values for the invariants $\Delta_{11} = 3(c_{12} - c_{66})/(c_{12} + 2c_{12})$:

	NaCl	KCl	NaCN	KCN	LiH	Li$_2$O	LiF
Δ_{11}	0.010	0.031	0.78	0.72	-0.95	-0.45	-0.26

	BeO	MgO	BaO	AgCl
Δ_{11}	-0.24	-0.39	0.*l*14	0.81

The largest effects appear in the cyanides and in AgCl, in which the strongly aspheric cyanide ions and the highly polarizable silver ion respectively, bring Δ_{11} close to the liquid value $\Delta_{11} = 1$. This is also directly seen in the highly plastic behavior of these crystals. In contrast, one finds negative Δ_{11} in crystals with cations and anions of low atomic number. These are to be interpreted as the effects of a strong covalent bonding content. The smallest value is observed in LiH.

As an example of the just discussed application of empirical rules, we will attempt to estimate the elastic constants of Na$_2$O, a substance crystallizing in a flourspar lattice and not easily produced in the form of a large single crystal. The necessary data come from the Landolt–Börnstein compilation and from the data banks of the lattice constants.

At first we assume that Na$_2$O possesses a similar S-value as Li$_2$O, namely $233.1 \cdot 10^{-20}$Nm. The molecular volume of Na$_2$O is $42.97 \cdot 10^{-30}$m^3. Hence, $C(\text{Na}_2\text{O}) \approx 5,43 \cdot 10^{10}Nm^{-2} = (c_{11} + c_{12} + c_{66})/3$. The deviation from the Cauchy relations Δ_{11} is taken from the relationship $\Delta_{11}(\text{Na}_2\text{O})/\Delta_{11}(\text{NaF}) \approx \Delta_{11}(\text{Li}_2\text{O})/\Delta_{11}(\text{LiF})$. The experimental values are $\Delta_{11}(\text{NaF}) = -0.08$, $\Delta_{11}(\text{Li}_2\text{O}) = -0.45$ and $\Delta_{11}(\text{LiF}) = -0.26$, furthermore, $\Delta_{11}(\text{Na}_2\text{O}) \approx -0.14$. For c_{66}/c_{11} we assume the value 0.29 measured in Li$_2$O as well as in NaF. From the three values for C, Δ_{11} and c_{66}/c_{11} we then obtain $c_{11}(\text{Na}_2\text{O}) \approx 10.80$, $c_{12} \approx 2.33$ and $c_{66} = c_{44} \approx 3.13 \cdot 10^{10}$Nm^{-2}. From experiences gathered so far, the actual values can deviate by about 10% from these estimates.

Another path uses the rule that the *S*-values of chemically similar constituents differ only by a small amount. We consider, for example, a hypothetical substance $A = \text{Na}_2\text{CaF}_2\text{O}$ and expect $S(A) \approx 2S(\text{NaF}) + S(\text{CaO}) \approx S(\text{CaF}_2) + S(\text{Na}_2\text{O})$. With $S(\text{NaF}) = 123$, $S(\text{CaO}) = 339$ and $S(\text{CaF}_2) = 328$ one finds $S(\text{Na}_2\text{O}) \approx 257 \cdot 10^{-20}$Nm, a value exceeding the one assumed above by about 10%.

More exact predictions are achieved with little effort when one investigates specimens of pressed fine grained powder rather than single crystals. For example, one can easily determine the two possible sound velocities of such isotropic substances, namely the pure longitudinal wave and the pure transverse wave which are coupled to the constants c_{11} and $c_{44} = c_{66}$ respectively, from the resonance frequencies of plane parallel plates or even measure the volume compressibility in a simple arrangement. With the aid of such experimental average values in combination with the estimates discussed above, one can, at least with cubic crystals, almost always come to rather useful predictions (see also Section 11, Exercise 25).

We now want to briefly address the testing of bonding properties with the help of the *S*-values (units: [10^{-20}Nm]). Let us again inspect the *S*-values of Na_2O. Since the properties of Na_2GeO_3 and GeO_2 are known, one can check the relation $S(Na_2GeO_3) \approx S(GeO_2) + S(Na_2O)$. Inserting the experimental values gives $466 \approx 739$ (for GeO_2 in the high pressure modification of the rutile-type) or about 200 (for GeO_2 in the α-quartz-type)$+S(Na_2O)$. It is obvious that the Ge-O bond in Na_2GeO_3 is in no way equivalent to the bond in the high pressure modification of GeO_2.

7.1.2.3 **Thermoelastic and Piezoelastic Properties**

The thermal energy content of a solid expresses itself mainly in the spectrum of the lattice vibrations and in the excitations of atomic and molecular states. The rise in amplitude of the lattice vibrations with increasing temperature not only causes a change in the mean separation between particles and hence the thermal expansion, but also a change in the interaction potential. This means, that apart from the consequences of excitation, it may be expected that the elastic properties are affected by the temperature dependence of the separation r_{ij} of the particles and also by the effective coefficients of the potential terms, in particular the repulsive potential and the van der Waals potential. The change of the elasticity tensor with temperature is described, at least in a limited temperature interval, by the tensor $\{T^*_{ijkl}\} = \{dc_{ijkl}/dT\}$ which possesses the symmetry properties of the elasticity tensor. However, for the discussion of thermoelastic properties, the logarithmic derivatives of the elastic constants $T_{ij} = d \log c_{ij}/dT$ have gained acceptance, which just like the elastic constants c_{ij} do not represent tensor components. We will use these quantities, which designate the relative change of the elastic constants per Kelvin in what is to follow. With a suitable temperature factor as, for example, the Debye temperature they become dimensionless and hence assume the tensor character. We will return to this point latter.

From the relationship $c_{ij} = F_{ij} \cdot r_{ij}^4$ given above, one obtains for ionic crystals $T_{ij} = d \log F_{ij}/dT - 4d \log r_{ij}/dT$. In cubic crystals such as the alkali halides, the second term corresponds to the negative four-fold linear thermal expansion α_{11}, for which experimental values of around $40 \cdot 10^{-6} K^{-1}$ exist. The constant T_{11} is about $-0.80 \cdot 10^{-3} K^{-1}$. This means that the change of the longitudinal resistance c_{11} with temperature is here more strongly determined by the influence of the temperature on F_{11}, hence, in particular on the effective exponent of repulsion and on the fraction of van der Waals bonds than on the separation of the ions. The change of F_{44} is made far less noticeable by the constants T_{44} describing the influence of the temperature on the shear resistance c_{44}. Thus the alkali halides demonstrate that thermoelastic properties are closely correlated with thermal expansion, but by no means can they

alone be attributed to this. Further details are described in the literature (for example, Haussühl 1960).

In the following we present the more important empirically found rules for thermoelastic behavior.

1. The T_{ij} are, with a few exceptions, always negative, except close to a higher order phase transformation. Its order of magnitude in stable crystals ranges from $-0.01 \cdot 10^{-3} \mathrm{K}^{-1}$ (diamond) to about $-5 \cdot 10^{-3} \mathrm{K}^{-1}$ (organic molecular crystals as, for example, benzene). The anisotropy of T_{ij} can be considerable.

2. The T_{ij} begin at absolute zero with vanishingly small values and with rising temperature take on increasingly negative values ($dT_{ij}/dT < 0$).

3. When approaching a strong 1. order phase transformation as, for example, the melting point, no particularly noticeable anomalies are observed until shortly before the transformation.

4. In isotype crystal series T_{ij} take on characteristic values. For example, crystals of NaCl-type and of CsCl-type possess strongly different T_{ij}. If symmetric ions are substituted by less symmetric ones, then significant deviations appear (for example, the substitution of K or Rb by NH_4 or CH_3NH_3; substitution of A subgroup elements by B subgroup elements).

5. The value of T_{ij} in isotype ionic crystals decreases with increasing charge (for example, $|T_{ij}(\mathrm{MgO})| < |T_{ij}(\mathrm{LiF})|$).

6. In isotypes or structurally and chemically related ionic crystals, those species with heavy particles exhibit normally a larger value of T_{ij} (for example, alkali halides, alums, sulfates, nitrates, phthalates, among others). Exceptions: with increasing solidification, for example, in organic crystals or in the sequence chlorate-bromate-iodate.

7. A general elastic isotropization or a reduction in the deviations from the Cauchy relations with increasing temperature is not observed.

8. The type of bonding is mirrored in the thermoelastic behavior:
   $|T_{ij}(\text{covalent})| < |T_{ij}(\text{ionic})| < |T_{ij}(\text{van der Waals})|$ at comparable average elastic resistance (C-value).

9. Characteristic thermoelastic anomalies appear close to second and higher order phase transformations, which can be attributed to certain transformation mechanisms (for example, rotative-librative; order-disorder; ferroelastic, ferroelectric and ferromagnetic phenomena).

10. In a large collective of crystals one finds a distinct correlation between thermoelastic properties and thermal expansion as, for example, between T_{ij} and α_{ij} ($T_{ij} \sim -\alpha_{ij}$) in rhombic crystals. The same sign for

T_{ij} and α_{ij} appears seldom which points to partly different causes of the anharmonicity.

11. The anisotropy of T_{ij} in cubic crystals, expressed by the ratio of longitudinal effects along [011] and [100], thus T'/T_{11} with $c' = (c_{11} + c_{12} + 2c_{44})/2$, takes on structure typical values. For example, NaCl-type including oxides: $T'/T_{11} \approx 0.60 \pm 0.05$; CsCl-type: $T'/T_{11} \approx 1.70 \pm 0.05$.

12. The invariants $T^* = \log C/dT$ with $C = (c_{11} + c_{22} + c_{33} + c_{44} + c_{55} + c_{66} + c_{12} + c_{13} + c_{23})/9$ and $z = d(\Delta/C)/dT$ with $\Delta = (c_{12} + c_{13} + c_{23} - c_{44} - c_{55} - c_{66})/3$ = average deviation from the Cauchy relations, take on similar values in different isotype series with equivalent ions. T^* drops to about one quarter when the ionic change is doubled. z also exhibits lower values.

As hinted above, when one now multiplies T_{ij} with the Debye temperature, which can be estimated from the elastic data, the range of variability of T_{ij} is reduced considerably, because elastically harder substances exhibit lower T_{ij}-values and larger C-values than softer substances. To what extent the general discussion can thereby be simplified is not yet decided, because the Debye temperatures must be calculated from the elastic data in the low temperature range and often these cannot be extrapolated with sufficient accuracy from the values measured at substantially higher temperatures. Whether one succeeds, with these dimensionless data, in setting up rules for thermoelastic properties similar to those for the S-values requires more detailed inspection.

Furthermore, we note that the mentioned rules also apply qualitatively in collectives of chemically related crystal types. Groups of substances with H-bridge bonding, however, often show a strong scattering in their thermoelastic constants due to the large variability of the binding strength (examples: carbonic acids and their salts; α and β alums). Tables 12.17 to 12.19 present experimental values of elastic properties of some of the substances discussed here.

Similar rules also exist for the piezoelastic constants $P_{ij} = dc_{ij}/dp$, where p is the hydrostatic pressure. These quantities are dimensionless. They exhibit similar regular traits as the thermoelastic constants, however, with opposite sign. In general, one can say that an increase of hydrostatic pressure is equivalent to a decrease in temperature. For example, often a phase transformation initiated at normal pressure by dropping the temperature can also be set into motion by increasing the pressure at normal temperature. An especially impressive property is shown by the pressure dependence of the reciprocal volume compressibility dK^{-1}/dp, which in almost all substances, virtually independent of structure and chemical constituents, assumes a value between approximately 4 and 6. Large deviations appear only in the region of phase transformations. This comparatively easy to measure quantity is thus suited

to the detection of a phase transformation, all the more, because a deviation from normal behavior is recognizably far removed from the transition temperature and from the transition pressure, and finally the measurements can also be carried out on very small probes.

With continuing advances in automation and miniaturization of measurement methods one can anticipate that in the near future the pool of data on physical properties will grow substantially so that the rules already formulated will become firmly cemented and new relationships in compliance with the laws will be found.

7.2
Phase Transformations

All crystal types investigated so far exhibit the phenomena of phase transformation during a transition through a certain temperature- or pressure range. If during this process a homogeneous crystal transforms into another homogeneous substance in the physical-chemical sense, as for example, in congruent melting or in the transformation of metallic tin in grey tin, then we talk of a homogeneous phase transformation. If, on the other hand a crystal breaks down, for example, during heating, into different components associated with many homogeneous substances, as, for example, in the dehydration of gypsum, then we are dealing with a heterogeneous phase transformation. At this point we will only concern ourselves with homogeneous phase transformations of the type solid–solid.

The phase transformations (PT) that interest us are firstly specified by the structure of the initial phase (mother phase) and the resulting phase (daughter phase). The processes involved in the rearrangement of the particles to form the daughter phase (transformation kinetics) can be of a diverse nature. It will be the aim of further research to elucidate just these processes occurring in the atomic range to gain a deeper understanding of the phenomena.

At first we recognize the phase transformation by certain erratic changes in macroscopic properties. In many cases a PT is observed visually or microscopically as a result of changes in the index and the formation of cracks which cloud the appearance of the crystal. In other cases, gross changes in the thermal, electrical and elastic properties can occur. On the other hand, a number of PTs can only be detected with sensitive measurement techniques. This applies, for example to most ferromagnetic, ferroelectric and the so-called order–disorder transformations as well as the just recently discovered incommensurable phases. In the latter, the periodic lattice structure motif is superimposed with a variation of periodic structure not compatible with the lattice periodicity in distinct directions. Table 7.3 presents some typical examples of phase transformations. The PTs can be classified according to various aspects.

Table 7.3 Examples of phase transitions at standard pressure. T_0 equilibrium temperature of the phases I and II. RG: space group.

Phase I ($< T_0$) Phase II ($> T_0$)	T_0 [K] $|\Delta V/V_{II}|$ ΔQ [Jg^{-1}]	Differences in physical behavior	RG I II	Transition kinetics Structural type of transition Thermodynamic type of transition
Graphite (C) Diamond (C) (metastable)	1200*) 0,54 158	large	P6$_3$/mmc Fd3m	slow reconstruction 1st order
β-Fe γ-Fe**)	1183 $2 \cdot 10^{-2}$ 16,5	small	Im3m Fm3m	fast dilative–martensitic 1st order
α-Fe β-Fe	1033 – 90	α phase ferromagnetic	Im3m Im3m	fast order–disorder strongly 2nd order
α-CsCl β-CsCl	743 0,16 22,4	large	Pm3m Fm3m	slow dilative–martensitic 1st order
α-Quartz β-Quartz	847 $< 10^{-6}$ 12,1	α phase longitudinal piezoelectric effect	P3$_1$2 P6$_2$2	fast displacive strongly 2nd order
β-NaCN γ-NaCN	284 $1,2 \cdot 10^{-2}$ 48	γ phase anomal elasticity	Immm Fm3m	fast rotatory order–disorder strongly 2nd order, weakly 1st order

Table 7.3 (continued)

γ-BaTiO$_3$	393	γ phase	P4mm	fast
δ-BaTiO$_3$	$< 10^{-5}$	ferroelectric	Pm3m	displacive order–disorder
	0,84			strongly 2nd order
α-Nb$_3$Sn	18,05	α phase	Pm3m	fast
β-Nb$_3$Sn	–	supraconducting	Pm3m	order–disorder
	> 0			2nd order
α-Rb$_2$Hg(CN)$_4$	398	α phase	R$\bar{3}$c	fast
β-Rb$_2$Hg(CN)$_4$	$1,5 \cdot 10^{-2}$	ferroelastic	Fd3m	displacive
	1,03			strongly 2nd order
α-TlAl(SO$_4$)$_2 \cdot$ 12H$_2$O	≈ 360	all	Pa3	upon activation by touching
β-TlAl(SO$_4$)$_2 \cdot$ 12H$_2$O	$0,5 \cdot 10^{-2}$	properties	Pa3	reconstruction, $\beta \to \alpha$ irreversible
(metastabil)	0,8			1st order
α-CaCO$_3$ (Aragonite)	–	all	Pnam	upon heavy mechanical stress, slow
β-CaCO$_3$ (Calcite)	$7,5 \cdot 10^{-2}$	properties	R$\bar{3}$c	reconstruction, $\beta \to \alpha$ irreversible
	2			1st order
α-Li$_2$Ge$_7$O$_{15}$	284	α phase	Pmm2	fast
β-Li$_2$Ge$_7$O$_{15}$	$< 10^{-4}$	pyro- and	Pmmm	displacive order–disorder
	0,1	ferroelectric		strongly 2nd order
α-TGS***)	322	α phase	P2$_1$	fast
β-TGS	$< 10^{-4}$	pyro- and	P2$_1$/m	displacive order–disorder
	1,94	ferroelectric		strongly 2nd order

*) The transition diamond $\to$ graphite can easily be observed above this temperature.

**) The lowest-temperature stable phase is usually denoted α or I, while the higher-temperature phases are subsequently denoted β, γ, δ or II, III, IV.

***) TGS: Triglycine sulfate, CH$_2$NH$_2$COOH)$_3 \cdot$ H$_2$SO$_4$.

Thermodynamic considerations stood in the forefront for a long time. If two phases are in thermodynamic equilibrium then they must possess the same values for the free enthalpy (pro mole) under the given auxiliary conditions. As an example, we consider the case of constant mechanical stresses, hence, also constant hydrostatic pressure, constant electric and magnetic fields and constant temperature. As we saw in Section 5, the Gibbs free enthalpy G assumes a minimum under isobaric, isagric, and isothermal conditions ($\Delta G = 0$; minimum from the point of view of stability). If both phases I and II are in equilibrium, then $G_I = G_{II}$. From this condition one obtains, for example, for the simple special case of hydrostatic pressure and no electric and magnetic field strengths, the Clausius–Clapeyron relation

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta Q}{T \Delta V},$$

where ΔQ is the transformation enthalpy, T is the equilibrium- or transformation temperature and ΔV is the change of volume in the transition from I to II. As proof one makes use of the expansion

$$G = G_0 + \frac{\partial G}{\partial p} \Delta p + \frac{\partial G}{\partial T} \Delta T$$

and the relations

$$\frac{\partial G}{\partial p} = V \qquad \text{and} \qquad \frac{\partial G}{\partial T} = -S.$$

The curve dp/dT describes the progress of the transformation pressure as a function of temperature and vice versa (vapor–pressure curve). If we cross from phase I to phase II by increasing the temperature, for example, then this is only possible by supplying energy. In equilibrium, ΔQ is the amount of energy required for the transformation. It is always positive, i.e., energy must always be supplied in a transition from a low temperature- to a high temperature phase, provided one stays close to equilibrium. The deeper background for this is the second law of thermodynamics, which in this case demands an increase in entropy ($S_{II} > S_I$). This means that the internal energy of the high temperature phase is higher than that of the low temperature phase.

If we work with uniaxial mechanical stresses instead of hydrostatic pressure and at the same time allow the action of electrical and magnetic fields then instead of the Clausius–Clapeyron relation one obtains a more complicated relationship, which we will not pursue any further at this point.

Crystals can be roughly divided into two groups on the basis of their different transformation enthalpies. The first group has easily measurable ΔQ-values of the order of a few percent of the lattice energy and more (lattice energy = formation enthalpy from the isolated lattice particles); in contrast,

the ΔQ-values of the second group are hardly or virtually not measurable. Intermediate substances are comparatively seldom. The transformations of the first group are termed *first-order transformations*, and those of the second as *second-order transformations*. A more exact definition states that in first-order transformations the first derivatives of a thermodynamic potential with respect to temperature or pressure (or another inducing quantity) exhibit a discontinuity. In second-order transformations the first derivatives show a continuous behavior, while the second and higher derivatives exhibit discontinuities. This formal classification appears quite elegant although it only captures a part on the transformations. In particular, the theory developed by Landau (1937) allows a number of general formulations concerning certain types of transformations, primarily those of second order. In this connection, an important role is played by the loss of symmetry elements of the mother phase during the phase transition leading to a characteristic change of certain tensor properties. The general discussion involves the variation ΔG of the Gibbs free energy on approaching the transformation point as a function of the inducing quantities. In the forefront is the behavior of so called *order parameters*, which are coupled to the interactions driving the transformations.

A crystallographic classification of PTs on the basis of structural aspects was proposed by Buerger (1948, 1951). Buerger distinguishes between four groups:

   I. Transformations of the first coordination sphere,

  II. Transformations of the second coordination sphere,

 III. Order–disorder transformations,

 IV. Transformations of the bonding type.

If the kinetics of transformation proceed hesitantly, as in all cases requiring an activation energy, then we are mainly dealing with crude structural changes. These phase transformations were called *reconstructive* by Buerger. Among these, in particular, most first-order transformations. If the structural difference of phases I and II is caused by small displacements of the particles, then the transformation is called *displacive*. In the case of homogeneous deformations, as for example, in martensitic PT, one speaks of *dilative transformations*, in transformations coupled with the activation of the rotational motion of groups of particles one speaks of *rotative transformations*. This classification has the great advantage that structural occurrences stand in the forefront in the treatment of transformations. From experience, one can set up common rules for transformation properties of the individual groups such as speed of the transformation process, reversibility and magnitude of the transformation enthalpy, which, for example, in the case of displacive PTs of the second coordination sphere, agree with some of the Landau rules for the second-order PTs.

The most important rules are cited as follows:

1. Reconstructive first-order PTs require a nucleation of the new phase. The work of nucleation prevents the prompt occurrence of the PT when exceeding the equilibrium conditions of temperature, pressure and electric or magnetic field strengths. This is due to the phenomena of under-cooling or over-heating of the mother phase in the region of the stable daughter phase. This delay of transformation can often extend over a long time, as is seen from the existence of certain minerals, for example, calcite, which were formed millions of years ago and in the mean time have not transformed into the more stable phase (here aragonite). The possibility to synthesis a variety of crystals, that cannot be produced under normal conditions is based on this behavior. The crystals are synthesized under high temperature and pressure conditions and then brought into a region outside their stability range by fast cooling or pressure relief without them breaking up (quenching). This applies, for example, to diamond synthesis.

In principle, some is true for first-order transformations induced by electric or magnetic fields.

As already alluded above, the transformation enthalpies are very large. Due to the often considerable change in volume, the homogeneity of single crystals seldom remains conserved. The new phase is created mostly in the form of small crystalline domains (crystallites) with irregular orientation. Quite often the crystals sustain many cracks and break into smaller pieces. One of the causes for this phenomenon is also the inhomogeneous temperature distribution. Likewise, the reverse transformation proceeds almost always strongly delayed (hysteresis).

2. Displacive, rotative, dilative (for example, also some martensitic) and order–disorder transformations occur without substantial delay when exceeding the equilibrium conditions. The reverse transformation commences very quickly. The observed small delays (hysteresis) are partly due to the defect structures of the crystal which can hinder transformation. The transformation enthalpies are extremely small. Single crystals of the mother phase pass over into single crystals of the daughter phase, whereby the formation of new defects hardly occurs, because virtually no change in volume takes place. The reverse transformation brings the crystal back to its initial situation, including the original defects. Finally, there exists almost always a close structural relationship between both phases. In particular, almost without exception, the space group of the low temperature phase is a subgroup of the space group of the high temperature phase. The classification of ferroelectric and ferroelastic PTs is based on this property (Aizu, 1969; Shuvalov, 1970).

A detailed analysis of the phenomena has shown that first-order reconstructive PTs are unequivocally identified by the criteria given here. Numerous phase transformations possess the characteristics mentioned under 2. with the

exception of the transformation enthalpy, which although small, is clearly ob-
served, as well as a certain weak hysteresis of a few degrees. Often these
transformations are also accompanied by a minute change in volume and an
optical clouding arising from microcracks. In these cases we conveniently
talk of a strong second-order or a weak first-order transformation, respec-
tively. The crucial difference as opposed to the first type of PTs consists of the
fact that these crystals possess an anomalous temperature- or pressure depen-
dence with respect to certain properties over a wide temperature- or pressure
range (or a corresponding range of the electric or magnetic field strength). Un-
der anomalous we understand a basically different behavior as we would ob-
serve in a collective of crystals which over a large range of the state variables
does not suffer such phase transformations. Especially strong are the anoma-
lies appearing in the temperature- and pressure coefficients of the elastic con-
stants (see, for example, Fig. 7.1). When approaching the phase boundary the
anomaly often amplifies itself to a singular behavior to then slowly normalize
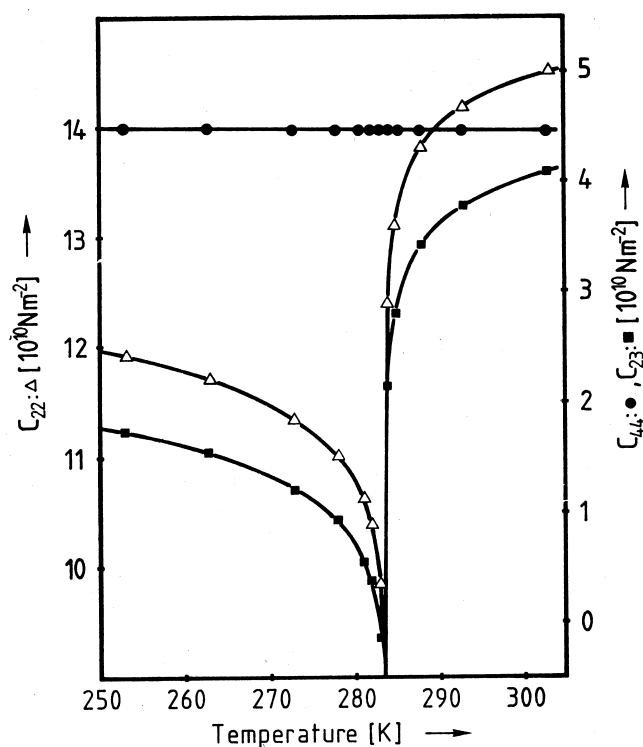

Figure 7.1 Anomalous temperature dependence of the elastic behav-
ior of $Li_2Ge_7O_{15}$ (c_{22} and c_{23} indicated) in a broad range of tempera-
tures around the transition temperature at 284 K (see also Fig. 4.5(a)
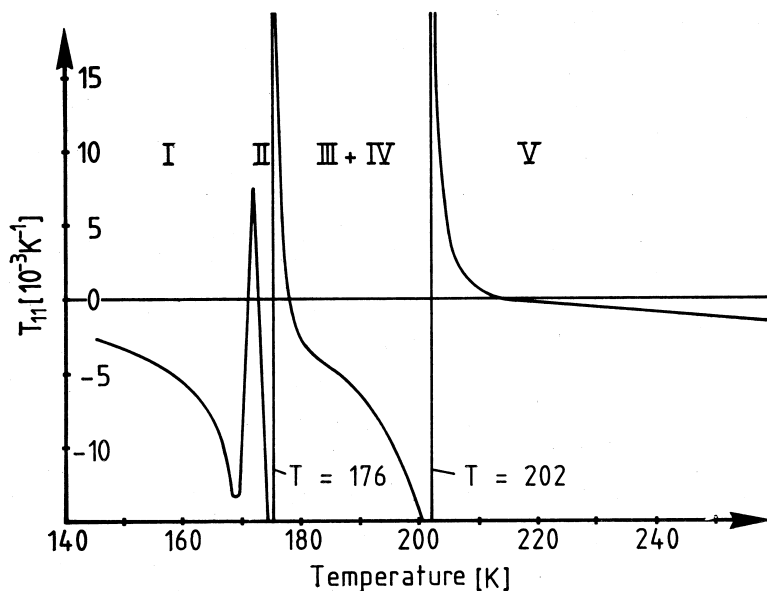and (b)).

Figure 7.2 Temperature dependence of the thermoelastic constant T_{11} of thiourea. Three regions of rapid sign inversion can be observed, corresponding to the transitions at $T_1 = 202$ K, $T_3 = 176$ K, and $T_4 = 173$ K. The phase transition ($III \leftrightarrow IV$) expected around 180 K from other experiments is barely visible in the behavior of T_{11}.

in the daughter phase farther removed from the phase boundary. The term λ-transformation was derived from this behavior. As far as the corresponding investigations on single crystals are concerned, there does not exist one single PT of this type which is not distinguished by such anomalies in elastic behavior already far from the transformation boundary. In contrast, in distinctive first-order PTs one does not observe such elastic anomalies even in the immediate vicinity of the stability limit. First-order PTs occur, in a manner of speaking, as a catastrophy without warning and lead to abrupt changes in properties.

Finally, there exists a series of crystals in which both types of transformation appear in certain ranges of the state variables. Within a specific temperature- or pressure range such crystals strive to attain a second-order transformation, however, before reaching the new phase may be destroyed by a first-order transformation. Furthermore, there also exists examples of several strong second-order PTs especially in organic crystals. Figure 7.2 presents the interesting case of thiourea ($CS(NH_2)_2$) which shows five PTs in the range between 168 and 300 K.

Furthermore, there also exists the possibility of carrying crystals over into another state by irradiation with light, whereby the external thermodynamic

variables do not change. This observed change in the electronic states of the atoms or molecules in crystals causes a change in the optical absorption behavior. In some cases these effects are directly seen as a change in color of the crystal (photochromatic effects). An interesting case of this type is illustrated by $Na_2FeNO(CN)_5 \cdot 2H_2O$, a rhombic crystal, which when irradiated with intense shortwave laser light at liquid nitrogen temperatures experiences a drastic change in the Mößbauer spectrum of the iron atoms over a period of many hours, and at the same time one observes a strong change in the optical absorption properties (Hauser et al., 1977). All such excitation states return to the initial state at higher temperatures due to thermal activation.

Related in a way to these phenomena is the desired effect of the formation of color centers, i.e., of excited states and specific defects, which in part rely on the existence of impurity atoms, (for example, color centers in the alkali halides, fluorite (CaF_2), smoky quartz, amethyst) by irradiation with high energy particles (γ-quantums, α-particles and so on). After intensive irradiation it may come to a partial destruction of the regular lattice structure, as for example, in the case of the isotropization of zircon ($ZrSiO_4$) and related types of crystals after radioactive irradiation. The energy stored in the damaged regions can be released by thermal activation, whereby the crystal, to a large part, again assumes its ordered structure.

A phase transition is interpreted by specifying a definite driving force resulting from a special interaction of the particles with one another. One anticipates that PTs based on analogous mechanisms and driving forces display similar traits of macroscopic transformation behavior and the same or a related functional dependence of the kinetics of transformation on the corresponding state variables (scaling).

As mentioned many times, the elastic properties play a fundamental role in all considerations on the stability of crystal phases. Let explain this aspect a little more. A crystal can only exist in a stable state at all, when its thermal energy is insufficient to deform large volume elements simultaneously into another, at least metastable arrangement, similar, for instance, to plastic deformation, which requires overcoming a certain threshold resistance. The elastic stability conditions are (see also Section 4.5.7.1):

All static and dynamic elastic resistances must exceed a certain minimum value given by the structural details and the thermal energy content of the crystal per unit volume. In particular, all the values of ρv^2 (ρ density, v velocity of sound) calculated from the elastic constants out of the elastodynamic basic equations for any arbitrary direction of propagation must lie above a certain limit. In the case of cubic crystals, these relations are:

$$c_{11}, \ c_{44}, \ c_{11} - c_{12}, \ c_{11} + 2c_{12} > 0.$$

For c_{12} this means

$$-c_{11}/2 < c_{12} < c_{11}.$$

In fact, one normally observes in crystals with very small shear resistances (for example, in cubic crystals c_{44} or $(c_{11} - c_{12})/2$) a tendency to transformation, especially then, when one approaches a temperature- or pressure range, in which the given coefficients dc_{ij}/dT and dc_{ij}/dp, effect a further reduction in the respective shear resistances (example, alkali cyanides). For similar reasons one can make rather confident predictions and also obtain clear details on the processes driving the transformation from a careful study of the temperature- and pressure dependence of the elastic constants wholly within the field of stability of strong second-order phase transitions.