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PHASE TRANSITIONS

Mechanism and heat evolution

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There are several approaches for the description of phase transitions (PT). leading to different classification schemes:

Approach	*Classification scheme by*
thermodynamic	order (after Ehrenfest)
kinetic	reversibility, quenchability, hysteresis
structural	relationship of crystallographic axes before and after PT
mechanistic	actual migration path of atoms during PT

The most important techniques for investigating PT include DTA and DSC, thermo-optical analysis, inelastic neutron scattering, IR and Raman spectroscopy and elastic X-ray and neutron diffraction. The latter, as dependent on the temperature, can give indications on the mechanism of PT. The appropriate application of these techniques is demonstrated on the example of, the polymorphism of KPO_3.

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Approaches to describe phase transitions

Several approaches are used to describe solid-state phase transitions [1].
1. The thermodynamic approach examines the change in the Gibbs free energy, G, as a function of parameters Z, such as temperature, pressure, magnetic field, electric field, etc. According to Ehrenfest [2], a phase transition is said to be of n^{th} order if n is the smallest number for which at least one

$$\frac{\partial^n (G)}{\partial (Z_i)^n}$$

is discontinuous.

This approach provides information on stability relations between different phases of a chemical compound and on the direction of phase transitions.
2. The kinetic approach considers the transition rate between polymorphous phases. The transition rate is strongly correlated with the activation energy required to transform one phase into another. If the activation energy is high, the phase transition is sluggish, has a high hysteresis, and can be easily quenched (e.g. $\alpha'-Ca_2SiO_4 \rightarrow \gamma-Ca_2SiO_4$). As the activation energy decreases, hysteresis and quenchability decrease (e.g. $\alpha-Ca_2SiO_4 \rightarrow \alpha'-Ca_2SiO_4$). Further, phase transitions are either reversible (enantiotropic) or irreversible (monotropic) (e. g. $\beta-Ca_2SiO_4 \rightarrow \gamma-Ca_2SiO_4$).
3. In the structural approach, the structures before and after a phase transition are compared.

According to Buerger [3, 4], phase transitions not involving the breaking of strong bonds are called displacive. In general, the crystal structures of two phases involved in a displacive phase transition show subgroup – supergroup symmetry relations. Required activation energies are low (e.g. $\alpha-Ca_2SiO_4 \rightarrow \alpha'-Ca_2SiO_4$; α-quartz → β-quartz). In contrast, a phase transition is called reconstructive if strong bonds are broken and the atoms are subsequently rearranged. Corresponding activation energies are higher than for displacive phase transitions
(e.g. ($\beta-Ca_2SiO_4 \rightarrow \gamma - Ca_2SiO_4$; quartz → coesite).

Displacive phase transitions are topotactic, i.e. the crystallographic axes of the two structures involved show well-defined orientation relationships. The degree of topotaxy decreases as the proportion of bonds broken during the transition increases (e.g. α-quartz → β-quartz – rhodonite → wollastonite-type (Mn,Ca)SiO_3 – quartz → coesite).

4. The mechanistic approach studies the actual migration paths of the atoms during a phase transition.

For phase transitions with a high degree of topotaxy (mainly displacive transitions), the actual migration paths are almost certainly nearly identical to the virtual migration paths proposed from a comparison of the two structures involved. As the degree of topotaxy decreases because more bonds are broken, the actual migration paths will increasingly deviate from the virtual migration paths and become more speculative. For non-topotactic (heterotactic) phase transitions such as quartz → coesite, even a reasonable guess of the actual atomistic mechanism is at present impossible.

Methods for the study of phase transitions

The most powerful methods for the study of phase transitions are:

1. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC). These two methods give information on the thermodynamics and the kinetics of a phase transition. The detailed shape of a heat effect as observed in a DTA and DSC curve gives hints on the atomistic mechanism of the corresponding transition.
2. Thermo-optical analysis (TOA) studies the changes in optical properties, such as birefringence and angles between optical axes, as functions of temperature. In addition to information on thermodynamic and kinetic properties, TOA gives information on symmetry changes.
3. IR and Raman spectra that are measured as a function of temperature, and in particular the softening of modes, give information on changes in lattice dynamics near a phase transition and changes in symmetry.
4. Inelastic neutron scattering and measurements of elastic constants give information on dynamic processes.
5. Elastic diffraction of X-rays and neutrons from crystals below and above the transformation temperature are used to determine the crystal structures of the two phases involved.

In favourable cases it is possible to correlate identical atoms in both structures and to calculate their virtual displacements [5]. From the size and anisotropy of the thermal ellipsoids, the amplitudes and directions of the thermal vibrations of the atoms can be deduced, giving indications on the transition mechanism.

Apt combinations of such methods are necessary for study, of all aspects of a phase transition.

Phase transitions of KPO_3

Potassium polyphosphate, KPO_3, is a suitable substance to demonstrate the kind of information that can be derived from the combination of various methods.

According to Jost [6], Jost and Schulze [7, 8] and Schmahl [5], there are four phase transitions between the crystalline phases of this phosphate:

$$T \xleftrightarrow{524\ \mathrm{K}} Z \xleftrightarrow{724\ \mathrm{K}} H' \xleftrightarrow{768\ \mathrm{K}} H \xleftrightarrow{922\ \mathrm{K}} HT \xleftrightarrow{1111\ \mathrm{K}} \mathrm{melt}$$

Although all four transitions are highly topotactic, they differ considerably in the shapes of their DTA effects, in their ΔH values, in hysteresis, and in quenchability. Four different order parameters have been deduced by comparing the structures, birefringence measurements, DTA curves, the X-ray intensities of specific reflections as a function of temperature, and the subgroup – supergroup symmetry relations. These order parameters are not only active at the critical temperatures of the phase transitions, but are also continuously active within the stability ranges of the phases. For the first-order phase transition $T \longleftrightarrow Z$, which has a hysteresis of about 15 K, the transition mechanism is shown to be a cooperative rotation of rigid $[PO_4]$ tetrahedra. This rotation involves an average migration length of 0.35 Å.

The average migration lengths of the other three phase transisitons are considerably smaller [5].

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Zusammenfassung – Phasenumwandlungen (PU) können unter verschiedenen Aspekten beschrieben werden, was zu unterschiedlichen Klassifikationen führt

Aspekt	*Klassifikation nach*
Thermodynamisch	Ordung (nach Ehrenfest)
Kinetisch	Reversibilität, Abschreckbarkeit, Hysterese
Strukturell	Beziehungen kristallographischer Achsen vor und nach der PU
Mechanistisch	Tatsächliche Bewegung der Atome während der PU

Zu den wichtigsten Untersuchungsmethoden der PU zählen DTA und DSC, thermooptische Analyse, inelastische Neutronenstreuung sowie IR- und Ramanspektroskopie und elastische Röntgen- und Neutronenbeugung in Abhängigkeit von der Temperatur. Aus letzteren können Hinweise auf den Mechanismus der Umwandlungen erhalten werden. Die geeignete Anwendung der Methoden wird am Beispiel des Polymorphismus des KPO_3 demonstriert.

РЕЗЮМЕ — Существует несколько подходов к описанию фазовых переходов (ФП), приводящих к различным классификационным схемам. Так, при термодинамическом подходе, фазовые переходы, согласно Эренфесту, разделяют по их роду. В кинетическом подходе классификация проводится согласно их обратимости, способности к закалке и наличию гистерезиса. При структурном подходе основным является взаимосвязь кристаллографических осей до и после ФП, тогда как при механическом — основным параметром является действительный путь смещения атомов во время фазового перехода. Среди наиболее важных методов исследования ФП являются метод ДТА и ДСК, термооптический анализ, жесткое рассеяние нейтронов, ИК спектроскопия и спектроскопия комбинационного рассеяния, а также диффракция нейтронов и мягкого рентгеновского излучения. Метод диффракции нейтронов, будучи зависим от температуры, может дать информацию о механизме ФП. Применение всех этих методов показано на примере полиморфизма KPO_3.