

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION  
COMMISSION ON HIGH TEMPERATURE  
AND SOLID STATE CHEMISTRY\*

## DEFINITIONS OF TERMS RELATING TO PHASE TRANSITIONS OF THE SOLID STATE

(IUPAC Recommendations 1994)

*Prepared for publication by*

J. B. CLARK<sup>1</sup>, J. W. HASTIE<sup>3</sup>, L. H. E. KIHNBORG<sup>4</sup>, R. METSELAAR<sup>5</sup> and  
M. M. THACKERAY<sup>1,2</sup>

<sup>1</sup>Division of Materials Science and Technology, CSIR, P.O. Box 395, Pretoria 0001, South Africa

<sup>2</sup>Present address: Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

<sup>3</sup>Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>4</sup>Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

<sup>5</sup>Lab. voor Fysische Chemie, Technische Universiteit Eindhoven, NL-5600 MB Eindhoven, Netherlands

\*Membership of the Commission during the period (1985–1993) when this report was prepared was as follows:

*Chairman:* 1989–93 J. Corish (Ireland); 1985–89 R. Metselaar (Netherlands); *Secretary:* 1991–93 G. M. Rosenblatt (USA); 1987–91 J. Corish (Ireland); 1985–87 P. W. Gilles (USA); *Titular Members:* J. F. Baumard (1985–93; France); J. Corish (1985–89; Ireland); J. D. Drowart (1987–93; Belgium); L. N. Gorokhov (1987–93; USSR); L. V. Gurvich (1985–87; USSR); J. W. Hastie (1987–93; USA); M. H. Rand (1985–87; UK); D.-S. Yan (1987–93; China); *Associate Members:* A.-M. Anthony (1985–89; France); H. P. Boehm (1991–93; Germany); C. Chatillon (1989–93; France); J. B. Clark (1985–91; South Africa); J.-P. Coutures (1985–87; France); J. Drowart (1985–87; Belgium); J. G. Edwards (1987–93; USA); L. N. Gorokhov (1985–87; USSR); J. Hastie (1985–87; USA); H. Hausner (1987–91; Germany); M. G. Hocking (1985–87; UK); L. H. E. Kihlborg (1985–91; Sweden); M. H. Lewis (1989–93; UK); J. Matousek (1985–93; Czechoslovakia); H. J. Matzke (1987–93; Germany); R. W. Ohse (1985–87; Germany); G. M. Rosenblatt (1985–91; USA); T. Saito (1989–93; Japan); M. M. Thackeray (1991–93; South Africa); G. van Tendeloo (1989–93; Belgium); G. F. Voronin (1989–93; USSR); H. Yanagida (1985–87; Japan); *National Representatives:* M. S. E. El-Sewefy (1985–87; Arab Republic of Egypt); E. J. Baran (1985–91; Argentina); P. Ettmayer (1986–93; Austria); B. G. Hyde (1987–93; Australia); O. L. Alves (1991–93; Brazil); D.-S. Yan (1985–87; China); E. Fitzer (1986–93; Germany); F. Solymos (1985–87; Hungary); A. P. B. Sinha (1985–87; India); G. V. Subba Rao (1989–93; India); G. De Maria (1985–93; Italy); S. Somiya (1985–87; Japan); C. H. Kim (1989–93; Korea); M. Badri (1985–87; Malaysia); W.-L. Ng (1989–93; Malaysia); K. J. D. MacKenzie (1987–93; New Zealand); F. M. de Abreu da Costa (1991–93; Portugal); M. A. Alario (1987–91; Spain); M. A. Alario Franco (1987–93; Spain); G. Bayer (1985–87; Switzerland); M. Kizilyalli (1987–93; Turkey); K. Spear (1989–93; USA); W. L. Worrell (1985–87; USA); D. Kolar (1987–93; Yugoslavia); M. M. Ristić (1985–87; Yugoslavia).

Names of countries given after Members' names are in accordance with the *IUPAC Handbook 1991–93*; changes will be effected in the *1994–95* edition.

---

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1994 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

# Definitions of terms relating to phase transitions of the solid state (IUPAC Recommendations 1994)

## *Synopsis*

This document provides definitions of phase transitions that relate specifically to the solid state. Various types of transition have been defined; they include: (i) structural transitions of the solid state, (ii) transitions related to the change in the state of matter, that is, from a solid phase to either a liquid or gaseous phase, or vice-versa, (iii) transitions related to changes in composition, (iv) metallurgical transitions, (v) transitions related to changes in the electronic structures of crystals, (vi) transitions that change thermodynamic properties or the disorder of a system, and (vii) liquid-crystal transitions.

## INTRODUCTION

This document, which provides definitions of phase transitions relating specifically to the solid state, is intended for the professional scientist but not necessarily for the specialist chemist, physicist or materials scientist. An attempt has been made to produce a set of concise definitions. Certain definitions have been expanded where clarification was considered necessary. In certain instances, definitions have been quoted directly from the literature, while in others, definitions have been modified or abridged to suit the document. A system of cross referencing has been used in which italicized terms refer to other entries where relevant information is available and where terms are known by more than one name.

A single phase is present if all the parts of a material system are identical in chemical composition, measurable properties, and physical state. A phase transition represents a change in the nature of a phase or the number of phases as a result of some variation in externally imposed conditions, such as temperature, pressure, activity of a component or a magnetic or electric field.

The term *phase transition* has been used broadly in the document to cover several types of phase changes: (i) structural transitions of the solid state, (ii) transitions related to the change in the state of matter, that is, from a solid phase to either a liquid or gaseous phase, or vice-versa, (iii) transitions related to changes in composition, (iv) metallurgical transitions, (v) transitions related to changes in the electronic structures of crystals, (vi) transitions that change thermodynamic properties or the disorder of a system, and (vii) liquid-crystal transitions.

Polymeric transitions are considered to fall outside the scope of this document and have therefore not been included. Also omitted from the document are certain obscure definitions that have appeared in the literature that have not yet been commonly accepted, such as the metallurgical terms "military transition" and "civilian transition".

## ACKNOWLEDGEMENTS

Comments/contributions made by the following persons during the compilation of this document are gratefully acknowledged:

S.C. Abrahams, R. Bareiss, V.V. Boldyrev, L. Brewer, B. Burton, J.B. Clark, J.D. Cox, P. Davidson, D.R. de Fontaine, J.D. Drowart, J.G. Edwards, P. Ford, P.W. Gilles, J.W. Goodby, J.B. Goodenough, Y. Haget, J.W. Hastie, J.M. Honig, R.A. Huggins, B.G. Hyde, L.H.E. Kohlborg, P. Kratochvíl, B. Legendre, J.W. Lorimer, A.D. McNaught, R.W. Munn, F.R.N. Nabarro, T.P. Radhakrishnan, C.N.R. Rao, J. Reedijk, R. Metselaar, J.C. Richer, P.W. Richter, G.M. Rosenblatt, R.S. Roth, Rustom Roy, D.K. Smith, K.E. Spear, G.V. Subba Rao, J.L. Tamarit, M.M. Thackeray, W.B. White, F.W. Wilburn and A.M. Zahra.

## DEFINITIONS OF TERMS

allotropic transition<sup>1,2</sup>

A transition of a pure element, at a defined temperature and pressure, from one crystal structure to another which contains the same atoms but which has different properties.

Examples: The transition of graphite to diamond, that of body-centred-cubic iron to face-centred cubic iron, and the transition of orthorhombic sulfur to monoclinic sulfur.

Alternative term: *allotriomorphic transition*.

allotriomorphic transition

See *allotropic transition*.

antiferroelectric transition

See *ferroelectric transition*, *ferroic transition*.

antiferromagnetic transition

See *ferroic transition*, *magnetic transitions*.

Bainite transition<sup>3</sup>

A term that is sometimes used in metallurgy for the *martensitic transition* that describes the transition between a face-centred-cubic lattice and a body-centred-tetragonal lattice.

Example: The transition between the face-centred-cubic lattice of austenite and the body-centred-tetragonal lattice of a martensite.

binodal curve<sup>4,5</sup>

The locus of the compositions of two co-existing phases on a temperature-composition phase diagram. On a temperature-composition plot, the binodal curve has a maximum at the upper *critical solution temperature*, and/or minimum at the lower *critical solution temperature*.

Alternative terms: *conodal curve*, *co-existence curve*.

See *conjugate solutions*.

cholesteric phase

See *liquid-crystal transitions*.

co-existence curve

See *binodal curve*.

commensurate-incommensurate transition<sup>1,6</sup>

A transition between two states having magnetic or crystallographic structures with a basic lattice and an imposed super-periodicity. In the commensurate (lock-in) state this super-periodicity is a simple rational multiple of the basic unit cell. In the incommensurate state the ratio of the super-periodicity repeat distance to the basic lattice repeat distance is irrational and may show continuous variation with variation in some degree of freedom (e.g. temperature, pressure, composition) of the system.

Example: The transition of  $\text{Rb}_2\text{ZnCl}_4$  from an incommensurate structure to a commensurate structure at the lock-in temperature,  $T_L$ , which is dependent on the crystal growth method and varies in the range 128 K to 190 K.

Note: A *commensurate-incommensurate transition* also occurs in liquid-crystal systems where there is an incommensurability in the packing of dimers in relation to monomers.

congruent transition<sup>7</sup>

A transition in which the two-phase equilibrium of *melting*, vaporization or allotropism of a compound involves phases of the same composition.

conjugate solutions<sup>2</sup>

Two solutions that co-exist in equilibrium at a given temperature and pressure and, at constant pressure (temperature), change their compositions and relative proportions with a variation of temperature (pressure). The term usually refers to two immiscible liquids, but it is also applicable to two immiscible solid solutions.

conodal curve

See *binodal curve*.

conode

The boundary curve on a temperature-composition phase diagram joining the compositions of independent co-existing phases.

consolute point<sup>8</sup>

See *critical solution point*.

continuous precipitation<sup>9</sup>

A diffusional reaction in a multi-component system in which atoms are transported to the growing nuclei by diffusion over relatively large distances in the parent phase and during which the mean composition of the parent phase changes continuously towards its equilibrium value.

Alternative term: *nucleation and growth*.

continuous transition

See *second-order transition*.

cooperative transition<sup>8</sup>

A transition that involves a simultaneous, collective displacement or change of state of the atoms and/or electrons in the entire system.

Examples: An *order-disorder transition* of atoms or electrons, as in an alloy, a ferromagnet or superconductor; a *Jahn-Teller* or *ferroic transition*; a *martensitic transition*.

cotectic<sup>8</sup>

The conditions of pressure, temperature, and composition under which two or more solid phases crystallize at the same time from a single liquid over a finite range of decreasing temperature.

critical solution composition

See *critical solution point*.

critical solution point<sup>10</sup>

The point, with coordinates critical solution temperature and critical composition, on a temperature-composition phase diagram at which the distinction between co-existent phases vanishes. In solid-solid, solid-liquid and liquid-liquid systems both upper and lower *critical solution temperatures* and corresponding *critical solution compositions* can occur.

Alternative term: *consolute point*.

critical solution temperature

See *critical solution point*.

crystallization<sup>8</sup>

The formation of a crystalline solid from a solution, melt, vapor or a different solid phase, generally by the lowering of the temperature or by evaporation of a solvent.

decomposition<sup>11</sup>

The breakdown of a single phase into two or more phases. The term applies also to other chemical entities such as a normal molecule and a reaction intermediate.

diffusional transition

A transition that requires the rearrangement of atoms, ions, or molecules in a manner that cannot be accomplished by a cooperative atomic displacement; it may require the movement of atoms, ions, or molecules over distances significantly larger than a unit cell.

Example: The transition of graphite (hexagonal sheets of three-coordinated carbon atoms) to diamond (infinite three-dimensional framework of four-coordinated carbon atoms) at high temperature and pressure.

diffusionless transition

A transition that does not involve long-range diffusion of atomic species over distances significantly greater than a typical interatomic distance.

dilatational (dilatational) transition<sup>12,13,14</sup>

A transition in which the crystal structure is dilated (or compressed) along one (or more) crystallographic direction(s) while the symmetry about that direction is retained.

Examples:

(i) The transition of a CsCl-type structure to a rock salt structure in which dilation occurs along the three-fold axis.

(ii) The transition at  $T_D$  in quenched NiS in which volume expansion occurs without change of symmetry on going from a metallic state ( $T > T_D$ ) to a semiconducting state ( $T < T_D$ ).

discontinuous precipitation<sup>9</sup>

A diffusional reaction in a multi-component system in which structural and compositional changes occur in regions immediately adjacent to the advancing interface. The parent phase remains unchanged until swept over by the interface; the transition is complete in regions over which the interface has passed.

Alternative term: *nucleation and growth*.

discontinuous transition

See *first-order transition*.

displacive transition<sup>1,12,13,14,15</sup>

A transition in which a displacement of one or more kinds of atoms or ions in a crystal structure changes the lengths and/or directions of bonds, without severing the primary bonds.

Examples: The transitions of the low-temperature polymorphs of  $\text{SiO}_2$  (quartz, tridymite and cristobalite) to their respective high-temperature polymorphs, which involve distortions or rotations of the  $\text{SiO}_4$  tetrahedra. Also *Jahn-Teller* and *ferroic transitions*.

disproportionation

A *reversible- or irreversible transition* in which species with the same oxidation state combine to yield one of higher oxidation state and one of lower oxidation state.

Example:  $3\text{Au}^+ \rightarrow \text{Au}^{3+} + 2\text{Au}$

The term also applies to an internal oxidation-reduction process as occurs, for example, among the iron atoms of  $\text{CaFeO}_3$ , where  $2\text{Fe}^{4+} \rightarrow \text{Fe}^{(4\delta)+} + \text{Fe}^{(4+\delta)+}$ , at Fe subarrays on lowering the temperature.

dissolution<sup>11,16</sup>

The mixing of two phases with the formation of one new homogeneous phase (i.e. the solution).

enantiotropic transition<sup>8,15</sup>

See *polymorphic transition*.

Note: In liquid crystal systems this term refers to a liquid crystal to *liquid crystal transition* that occurs above the melting point.

euatmotic reaction<sup>17</sup>

An isothermal, reversible reaction between two (or more) solid phases during the heating of a system as a result of which a single vapour phase is produced.

eutectic reaction<sup>2</sup>

An isothermal, reversible reaction between two (or more) solid phases during the heating of a system, as a result of which a single liquid phase is produced.

eutectoid reaction<sup>2</sup>

An isothermal, reversible reaction between two (or more) solid phases during the heating of a system, as a result of which a single, new solid phase is produced.

exchange-inversion transition<sup>18</sup>

A transition between antiferromagnetic and ferromagnetic coupling between two subarrays of magnetic atoms.

Example: Ordered FeRh changes from antiferromagnetic to ferromagnetic coupling with the simple cubic Fe array in a *first-order transition*.

ferrimagnetic transition

See *ferroic transition, magnetic transitions*.

ferroelastic transition<sup>1,19,20</sup>

A transition in which a crystal switches from one stable orientation state into another that is equally stable by the application of a mechanical stress along an appropriate direction.

See *ferroic transition*.

ferroelectric/antiferroelectric transition<sup>1,3,14,19</sup>

A transition from a ferroelectric to either another ferroelectric, or a paraelectric, or an antiferroelectric state.

Example: The transition of the low-temperature, cubic paraelectric BaTiO<sub>3</sub> to the high-temperature, tetragonal, ferroelectric form at 393 K.

Note 1: In an antiferroelectric transition individual dipoles become arranged antiparallel to adjacent dipoles with the result that the net spontaneous polarization is zero.

Note 2: Ferroelectric/antiferroelectric transitions also occur in the liquid-crystal state. These states are dependent on the alternating nature of dipoles between layers in the *smectic state*<sup>21</sup>.

See *ferroic transition*.

ferroic transition<sup>1,19</sup>

A general term for ferroelastic, ferroelectric, antiferroelectric, ferromagnetic, antiferromagnetic and ferrimagnetic transitions in which a suitable driving force switches a ferroic crystal from one orientation state, or domain state, to another.

Examples:

Ferroic class	Orientation state differ in	Switching force	Example
ferroelectric	spontaneous polarization	electric field	BaTiO <sub>3</sub>
ferroelastic	spontaneous strain	mechanical stress	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
ferromagnetic	spontaneous magnetization	magnetic field	Co

ferromagnetic transition

See *ferroic transition, magnetic transitions*.

first-order transition

A transition in which the molar Gibbs energies or molar Helmholtz energies of the two phases (or chemical potentials of all components in the two phases) are equal at the transition temperature, but their first derivatives with respect to temperature and pressure (for example, specific enthalpy of transition and specific volume) are discontinuous at the transition point, as for two dissimilar phases that coexist and that can be transformed into one another by a change in a field variable such as pressure, temperature, magnetic or electric field.

Example: The transition on heating CsCl to 752 K at which it changes from the low-temperature, CsCl-type structure to the high-temperature NaCl-type structure.

Alternative term: *discontinuous transition*.

freezing

The conversion of a liquid to a solid by lowering the temperature and/or the application of pressure.

glass transition<sup>1,3,14,24</sup>

A *second-order transition* in which a supercooled melt yields, on cooling, a glassy structure. Below the glass-transition temperature the physical properties vary in a manner similar to those of the crystalline phase.

Example: Lithium disilicate crystals melt at 1305 K; the melt can be supercooled to the *glass-transition temperature* at approximately 773 K below which the viscous liquid freezes to a rigid amorphous glass.

glass-transition temperature

The temperature at which the viscosity of the glass is  $10^{13}$  dPa s.

higher-order transition<sup>1,3</sup>

A general term used to describe a transition in which the first and second derivatives of the molar Gibbs energy or molar Helmholtz energy (or chemical potential) with respect to temperature and pressure are continuous, but derivatives of some higher order are discontinuous at the transition point.

Alternative term: *smooth transition*.

hysteresis<sup>3</sup>

The difference in temperature or pressure for the transition of one phase to another in the forward and reverse directions. It also refers to the corresponding difference in magnetic, electric or stress field in reversing the sense of magnetic, electric or strain polarization in ferromagnetic, ferroelectric or ferroelastic materials.

incongruent reaction

See *peritectic reaction*.

insertion reaction<sup>25,26</sup>

A general term given to a reaction involving the transfer of a guest atom, ion or molecule into a host crystal lattice.

See *intercalation reaction, topochemical reaction, topotactic reaction*.

intercalation reaction<sup>25,26</sup>

A reaction, generally reversible, that involves the introduction of a guest species into a host structure without a major structural modification of the host. In the strictest sense, intercalation refers to the insertion of a guest into a two-dimensional host; however, the term also now commonly

refers to one-dimensional and three-dimensional host structures.

Example: The insertion of lithium into layered  $\text{TiS}_2$



Alternative term: *insertion reaction*.

#### interphase transition

A transition that occurs at boundaries between phases.

Example: The precipitation of second phases or the initiation of new phase growth at an interface.

#### intrapphase transition

A transition that occurs within a phase.

Example: Initiation of phase growth at an intragranular feature, such as twin planes and dislocations in steels.

#### inversion point

The temperature (pressure) at which one polymorph of a solid phase changes into another at constant pressure (temperature).

See *polymorphic transition*.

#### irreversible transition<sup>3,24</sup>

A transition that changes the state of a system which cannot be readily reversed to restore the system to its original state.

Example: The conversion of  $\text{TiO}_2$  (*anatase*) to  $\text{TiO}_2$  (*rutile*).

#### Jahn-Teller transition<sup>1,3</sup>

A displacive crystal distortion to lower symmetry that cooperatively removes a localized - electron orbital degeneracy at an array of like atoms so as to leave the atoms in the centre of symmetry of their distorted sites.

Example: The crystallographic distortion in  $\text{Mn}_3\text{O}_4$ .

#### lambda transition<sup>3,14</sup>

A *second-order* or *higher-order transition*, in which the heat capacity shows either a discontinuity (second-order) or a vertex (higher-order) at the transition temperature.

Example: The transition at 846 K, accompanied by a finite change in specific heat capacity at constant pressure  $C_p$ , of the low-temperature polymorph of quartz to the high-temperature polymorph.

#### liquid-crystal transitions<sup>1,3,27</sup>

A liquid crystal is a molecular crystal with properties that are both solid- and liquid-like. Liquid crystals are composed predominantly of rod-like or disc-like molecules, that can exhibit one or more different, ordered fluid phases as well as the isotropic fluid; the translational order is wholly or partially destroyed but a considerable degree of orientational order is retained on passing from the crystalline to the liquid phase in a *mesomorphic transition*.

##### (i) transition to a nematic phase

A *mesomorphic transition* that occurs when a molecular crystal is heated to form a *nematic phase* in which the mean direction of the molecules is parallel or antiparallel to an axis known as the director.

##### (ii) transition to a cholesteric phase

A *mesomorphic transition* that occurs when a molecular crystal is heated to form a *cholesteric phase* in which there is simply a spiralling of the local orientational order perpendicular to the long axes of the molecules.



(iii) transition to a smectic state

A *mesomorphic transition* that occurs when a molecular crystal is heated to yield a *smectic state* in which there is a one-dimensional density wave which produces very soft/disordered layers.

liquidus<sup>2,8</sup>

A line on a binary phase diagram (or surface on a ternary phase diagram) that indicates the temperature at which *solidification* begins on cooling or at which *melting* is completed on heating under equilibrium conditions.

localized-itinerant transition<sup>3</sup>

A transition of either of two types:

- (a) a *Mott transition* (single-valent systems).
- (b) a small-polaron to itinerant-electron transition (mixed-valent systems).

lock-in state

See *commensurate-incommensurate transition*.

magnetic transition<sup>1,14,18,19</sup>

A transition between disordered and ordered arrays of atomic magnetic moments. Where the ordered phase has a net spontaneous magnetization,  $M_S$ , the magnetic-ordering temperature is called a Curie temperature,  $T_C$ ; where the net spontaneous magnetization of the ordered phase remains zero, the ordering temperature is called a Néel temperature,  $T_N$ . The temperature at which the two ferromagnetic subarrays of a ferrimagnet just cancel each other is called the compensation point.

Materials exhibit *ferromagnetic* behaviour when unpaired electron spins are aligned in parallel, *antiferromagnetic* behaviour when the alignment is antiparallel, and *ferrimagnetic* behaviour if the alignment of the spins is antiparallel with unequal numbers in the two orientations or if the spins are canted. Therefore, ferromagnetic, ferrimagnetic and weak ferromagnetic transitions involve a net magnetic moment change, whereas antiferromagnetic transitions have zero net magnetic moment change.

Note: Antiferromagnetic order below  $T_N$  may be complex; for example, canting of spins as in  $\text{GdFeO}_3$ , spiral-spin configuration as may occur in  $\text{MnO}_2$ , and amplitude modulation, as in some rare-earth metals.

martensitic transition<sup>1,3,14,28</sup>

A *diffusionless transition* (first studied in the steel alloy, Martensite), at constant composition, generated by coordinated atomic, ionic or molecular displacements over distances smaller than interatomic distances in the parent phase. The cooperative rearrangements of the crystal structure generally take place progressively by the movement of a two-dimensional interface through the solid.

Examples: The face-centred-cubic- to body-centred-tetragonal transition of iron containing some carbon; the transition of tetragonal  $\text{ZrO}_2$  to monoclinic  $\text{ZrO}_2$ .

massive transition<sup>1</sup>

A transition in which a crystal structure is changed into a new structure during cooling or heating, predominantly by interface-controlled reactions and the usual *nucleation and growth* characteristics associated with thermal diffusion.

melting

The conversion of a solid to a liquid by the application of heat and/or pressure.

Note: For a liquid crystal, *melting* occurs when the three-dimensional periodic structure of a solid collapses to give a liquid-crystal phase in which the molecules have orientational order, but not long range translational order.

mesomorphic transition<sup>8</sup>

A transition that occurs between a fully-ordered crystalline solid and an isotropic liquid. *Mesomorphic transitions* can occur (i) from a crystal to a liquid crystal (ii) from a liquid crystal to another liquid crystal and (iii) from a liquid crystal to an isotropic liquid.

See *liquid-crystal transitions*.

metal-insulator transition<sup>3</sup>

A transition characterized by a sudden change in electrical transport properties (conductivity) due to a reversible change from localized to itinerant behaviour of the electrons.

Example: The transition at 339 K in VO<sub>2</sub> where it changes from a high-temperature metallic behaviour to a low-temperature semi-conductor behaviour.

Alternative term: *metal-nonmetal transition*.

See *localized-itinerant transition*.

metal-nonmetal transition

See *metal-insulator transition*.

metamagnetic transition

An *antiferromagnetic to ferromagnetic transition* for  $H_{\text{applied}} > H_c$  and/or  $T > T_t$  where  $H_c$  and  $T_t$  refer to the critical magnetic field and transition temperature, respectively.

metastability

A term that describes the state of a phase in which an energy barrier considerably higher than  $kT$  must be surmounted before this phase can transform to a phase of lower molar Gibbs energy and molar Helmholtz energy, where  $k$  is the Boltzmann constant and  $T$  the thermodynamic temperature.

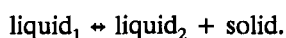
Note: In a thermodynamic sense, the equilibrium state is the state with the lowest molar Gibbs energy, a metastable state corresponds to a relative minimum in the molar Gibbs energy.

metatectoid reaction

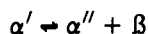
See *peritectoid reaction*.

monotectic reaction<sup>2</sup>

The *reversible transition*, on cooling, of a liquid to a mixture of a second liquid and a solid:

monotectoid reaction<sup>10</sup>

A reaction in a system containing two solid solution phases,  $\alpha'$  and  $\alpha''$  in which  $\alpha'$  decomposes into  $\alpha''$  and a new phase  $\beta$ :

monotectoid temperature

The maximum temperature at which a *monotectoid reaction* can occur.

monotropic transition

The *irreversible transition* from a metastable polymorphic form to the stable polymorph.

Example: The transition of metastable CaCO<sub>3</sub> (*aragonite*-type) to the stable CaCO<sub>3</sub> (*calcite*-type).

Note: For liquid crystals the term refers to a liquid crystal to *liquid-crystal transition* that occurs below the melting point and is revealed by supercooling of the crystal.

Morin transition<sup>3</sup>

A transition specific to  $\alpha\text{-Fe}_2\text{O}_3$  in which there is a change in the direction of the atomic magnetic moments in the antiferromagnetic state from parallel to perpendicular to the  $c$ -axis.

Alternative term: *spin-flop transition*.

morphotropic transition<sup>29</sup>

An abrupt change in the structure of a solid solution with variation in composition.

Mott transition<sup>30</sup>

A transition occurring only in "single-valent" systems from strongly correlated ( $U > W$ ) to weakly correlated ( $U < W$ ) electrons as a result of a change of bandwidth  $W$ .  $W$  reflects the strength of the interatomic interactions in a periodic array of like atoms and  $U$  is a measure of the intra-atomic interactions, i.e. the electrostatic energy involved in the creation of polar states by transferring an electron from one atom to the next, as shown schematically by the *disproportionation* reaction:



A  $U > W$  produces a magnetic semiconductor; a  $U < W$  gives rise to a metal (normally non-magnetic). Note also that  $U$  and  $W$  can be altered by changes in interatomic distances, brought about through temperature or pressure variations or by introducing an alloying element.

Alternative term: *Mott-Hubbard transition*.

Mott-Hubbard transition

See *Mott transition*.

nematic phase

See *liquid-crystal transitions*.

 $n$ -th order phase transition<sup>1,15</sup>

A transition in which the molar Gibbs energy (or chemical potential) and its  $(n-1)$ th-order derivatives are continuous, whereas the  $n$ th-order derivatives with respect to temperature and pressure are discontinuous at the transition point.

See *first-order transition*, *second-order transition*.

nucleation and growth<sup>3</sup>

A process in a *phase transition* in which nuclei of a new phase are first formed, followed by the propagation of the new phase at a faster rate.

See *continuous precipitation*, *discontinuous precipitation*.

order-disorder transition<sup>1,3,8,14,15</sup>

A transition in which the degree of order of the system changes. Three principal types of disordering transitions may be distinguished: (i) positional disordering in a solid, (ii) orientational disordering which may be static or dynamic and (iii) disordering associated with electronic and nuclear spin states.

Examples:

(i) The transition of  $\text{LiFeO}_2$ , with a tetragonal unit cell, in which the  $\text{Li}^+$  and  $\text{Fe}^{3+}$  cations are perfectly ordered on crystallographically non-equivalent octahedral sites to cubic  $\text{LiFeO}_2$  in which the  $\text{Li}^+$  and  $\text{Fe}^{3+}$  cations are distributed randomly over all the octahedral sites.

(ii) The transition of orthorhombic KCN to cubic KCN in which the  $\text{CN}^-$  ions become oriented in any of the eight [111] directions.

(iii) A *superconducting transition*.

order parameter

A normalized parameter that indicates the degree of order of a system. An order parameter of 0 indicates disorder; the absolute value in the ordered state is 1.

Peierls transition<sup>31</sup>

A *metal-insulator transition* in quasi one-dimensional solids that occurs as a result of a band gap opening up at the Fermi energy due to a displacive distortion of the regular array increasing the unit cell length, usually a dimerisation; the decrease in electronic energy outweighs the increase in lattice energy.

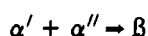
Example: The transition in methylethylmorpholinium tetracyanoquinodimethanide at 335 K.  
peritectic reaction<sup>2,8</sup>

An isothermal, reversible reaction between two phases, a liquid and a solid, that results, on cooling of a binary, ternary, .....,  $n$  system in one, two, .....,  $(n-1)$  new solid phases.

Alternative term: *incongruent reaction*.

peritectoid reaction<sup>2,8,10</sup>

An isothermal, reversible reaction in the solid state, that, on cooling of a binary, ternary, .....,  $n$  system, results in one, two, ....  $(n-1)$  new solid phases. For example, in a binary system containing two solids  $\alpha'$  and  $\alpha''$



Alternative term: *metatectoid reaction*.

peritectoid temperature

The maximum temperature at which a *peritectoid reaction* can occur.

phase

An entity of a material system which is uniform in chemical composition and physical state.

phase rule<sup>32</sup>

The number of degrees of freedom,  $F$ , that a system containing  $C$  components can have when  $P$  phases are in equilibrium, is given as:

$$F = C - P + 2$$

phase separation<sup>14</sup>

The process by which a single solid (liquid) phase separates into two or more new phases.

phase transition

A change in the nature of a phase or in the number of phases as a result of some variation in externally imposed conditions, such as temperature, pressure, activity of a component or a magnetic, electric or stress field.

plait point

A point in a ternary system with a binary *critical solution point*, at which *tie-lines* between co-existing phases became tangential to the *co-existence curve*.

plait point curve<sup>10</sup>

The locus of the *plait point* with temperature on a temperature-composition phase diagram.

plastic transition

A *first-order transition* that occurs when a low-temperature phase transforms to an orientationally-disordered high-temperature phase with a strong variation of enthalpy.

polymorphic transition<sup>15,33</sup>

A *reversible transition* of a solid crystalline phase at a certain temperature and pressure (the *inversion point*) to another phase of the same chemical composition with a different crystal structure.

Note: In a *liquid-crystal transition*, this term refers to phase changes in the *smectic state* or columnar discotic state.

**Examples:**

1. The transitions of  $\text{SiO}_2$  (quartz-type) at 1143 K to  $\text{SiO}_2$  (tridymite-type), and at 1743 K to  $\text{SiO}_2$  (cristobalite-type).
2. The transition of  $\beta\text{-AgI}$  (wurtzite-type structure) to  $\alpha\text{-AgI}$  (body-centred-cubic structure) at 418 K.

Alternative term: *enantiotropic transition*.

**polytypic transition**<sup>3,8</sup>

A transition of a crystalline structure into one or more forms which differ in the way identical layers of atoms are stacked.

Example: ZnS consists of two identical close packings, one of Zn atoms, the other S atoms, with the one displaced to the other along the c-axis through one-quarter of the layer spacing. In sphalerite-type ZnS the layers have the face-centred-cubic (ABC ABC) sequence, in wurtzite-type ZnS they have the hexagonal-close-packed (AB AB) sequence. The transition of sphalerite-type ZnS to wurtzite-type ZnS occurs at 1297 K.

**precipitation**<sup>11</sup>

The formation of a solid phase within a liquid phase.

**pressure-induced transition**<sup>3</sup>

A transition induced by a change of pressure.

Example: The room-temperature transition of CdS with a wurtzite-type structure, at 1.74 GPa, to CdS with a NaCl-type structure.

**reconstructive transition**<sup>3,12,13,14,15</sup>

A transition which involves a major reorganization of the crystal structure and a change of local topology, during which primary bonds are broken and reformed so that there is no immediate relationship between the crystal structures of the parent and product phases.

Examples: The transition of  $\text{Mg}_2\text{SiO}_4$  (*olivine*) to  $\text{Mg}_2\text{SiO}_4$  (*spinel*); the transition of diamond to graphite.

**recrystallization****(i) chemical**

The repeated *dissolution* and *precipitation* of a solid from a liquid solvent.

**(ii) metallurgical**

The process in which a crystalline solid with a high degree of disorder develops a new microstructure by the nucleation of relatively imperfection-free regions, and their propagation throughout the complete solid.

**reversible transition**<sup>24</sup>

A transition that returns a system directly to its original state by reversing the process that changed it.

**rotator phase transition**<sup>34</sup>

A transition from a fully-ordered crystal of globular or quasi-spherical molecules to a crystal that retains translational order but exhibits dynamic orientational disorder and is usually mechanically soft (plastic phase).

Example: The transition of  $\text{CBr}_4$  to a plastic phase which exists from 319 K to 365 K.

**second-order transition**<sup>1,3,14,15</sup>

A transition in which a crystal structure undergoes a continuous change and in which the first derivatives of the Gibbs energies (or chemical potentials) are continuous but the second derivatives with respect to temperature and pressure (i.e. heat capacity, thermal expansion, compressibility) are

discontinuous.

Example: The *order-disorder transition* in metal alloys, for example, CuZn.

Alternative term: *continuous transition*.

#### segregation<sup>1</sup>

The process that differentiates the composition at an interface or surface from the average or bulk composition.

Note: The composition of the segregated phases need not be uniform, for example, when concentration gradients are established in the phases.

#### semiconductor-metal transition<sup>3</sup>

Any transition from a semiconductor to a metallic state under the influence of a temperature or pressure change or both.

Examples:

- (i)  $\text{Ti}_2\text{O}_3$ : band-edge crossing in a semiconductor to semimetal transition.
- (ii) SmS: localized level crossing a band edge. In SmS hydrostatic pressure above the critical pressure  $P_c \approx 0.65$  GPa broadens the Sm-5d band to make the band edge cross the Sm-4f<sup>6</sup> level.
- (iii) A *localized-itinerant transition*.
- (iv) A *switching transition*.

#### shear transition

A *diffusionless transition* that involves a change of the shape of the unit cell by a process that can be described as shear.

#### smectic state

See *liquid-crystal transitions*.

#### smooth transition

See *higher-order transition*.

#### sol-gel transition

The transition of a suspension of solid particles in a liquid (sol) to an apparent solid, jelly-like material (gel).

#### solidification<sup>8</sup>

The transition of a liquid or gas into a solid.

#### solidus<sup>2</sup>

A line on a binary phase diagram (or a surface on a ternary phase diagram) that indicates the temperature at which a system becomes completely solid on cooling or at which melting begins on heating under equilibrium conditions.

#### solvus<sup>2</sup>

A line on a binary phase diagram (or a surface on a ternary phase diagram) that defines the limit of solid solubility under equilibrium conditions.

#### spin-flip transition

A rotation of electron spins, above a critical magnetic field,  $H_c$ , in an antiferromagnet from parallel to largely perpendicular alignment, relative to an applied magnetic field,  $H_a$ , for  $H_a > H_c$ .

#### spin-flop transition

See *Morin transition*.

spin-glass transition<sup>3</sup>

A *second-order transition* from a paramagnetic or ferromagnetic state to a spin-glass state in which spins from moment-bearing solute atoms become ordered randomly in a non-magnetic host such that the net magnetization of any region is zero.

Examples:

- (i) Au-Fe      (ii) Cu-Mn      (iii) Mo-Fe

spin-Peierls transition<sup>35</sup>

A magneto-elastic transition that occurs in quasi one-dimensional antiferromagnetic materials when the magnetic free energy decrease due to the formation of singlet spin pairs outweighs the increase in lattice free energy occurring as a result of the dimerisation of the regular array.

Example: The transition in tetrathiafulvalenium bis(dithiolene)cuprate at 12 K.

spinodal curve<sup>4,5</sup>

The boundary curve between metastable and unstable regions in a system with co-existing phases. It lies within the *binodal curve* and coincides with this curve at the *critical solution temperature* or temperatures.

spinodal decomposition<sup>1,36,37,38</sup>

A clustering reaction in a homogeneous, supersaturated solution (solid or liquid) which is unstable against infinitesimal fluctuations in density or composition. The solution therefore separates spontaneously into two phases, starting with small fluctuations and proceeding with a decrease in the Gibbs energy without a nucleation barrier.

spin-state transition<sup>3</sup>

An electronic transition from a high-spin state to a low-spin state, or *vice-versa*.

Example: With an increase in temperature  $\text{Co}^{3+}$  ions in  $\text{LaCoO}_3$  transform from a low-spin state ( $t_{2g}^6 e_g^0$ ) to the high-spin state ( $t_{2g}^4 e_g^2$ ).

strain-induced transition

A transition in a solid that is initiated by plastic strain.

stress-assisted transition<sup>1</sup>

A transition that takes place when an applied stress assists the transition to the new phase.

structural transition<sup>39</sup>

A *reversible* or *irreversible transition* that involves a change of the crystal structure.

Example: The transition of  $\text{NH}_4\text{Cl}$  at 469 K from a CsCl-type structure to a NaCl-type structure.

subgroup-supergroup transition<sup>3,40</sup>

A transition in which the space-group symmetry of the lower symmetry phase is a subgroup of that of the higher symmetry phase.

Example: The transition of the low-temperature polymorph of quartz characterized by space-group symmetry  $P3_12$  (trigonal), to the high temperature polymorph of quartz with space-group symmetry,  $P6_222$  (hexagonal).

Alternative term: *symmetry-breaking transition* (note: this term, strictly speaking, is no longer in use).

sublimation<sup>8</sup>

The direct transition of a solid to a vapour without passing through a liquid phase.

Example: The transition of solid  $\text{CO}_2$  to  $\text{CO}_2$  vapour.

superconducting transition<sup>19</sup>

A transition at the critical temperature,  $T_c$ , below which the resistance of electrical conductors becomes zero and magnetic flux is excluded.

Examples: The transitions of  $\text{Nb}_3\text{Sn}$ ,  $\text{Nb}_3\text{Al}$  and  $\text{V}_3\text{Si}$  to superconductors (15 K  $< T_c < 20$  K) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x \approx 0.2$ ) at 90 K.

switching transition<sup>3</sup>

A transition in semiconductive glasses in which, beyond a critical applied voltage, there is an avalanche breakdown of conducting electrons that causes local melting and hence local crystallization that gives metallic conductivity.

symmetry-breaking transition

See *subgroup-supergroup transition*.

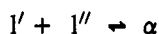
symmetry-conserving transition

A transition in which the cell dimensions and/or angles of the one phase differ from those in the other phase, but where the space-group symmetry is conserved.

Example: The transition of face-centred cubic Ce, upon cooling, to a face-centred cubic phase that is 10% denser. Upon cooling, enough contraction takes place to allow an overlap of the  $\text{fsp}^2$  configuration and the change from an isolated non-bonding magnetic f electron to a bonding non-magnetic electron pair.

syntectic reaction<sup>10</sup>

A reversible reaction that involves the conversion of two liquid phases,  $l'$  and  $l''$ , into a solid phase  $\alpha$  on cooling:



The maximum temperature at which this reaction can occur is the congruent melting point of the solid phase.

Example: The conversion of co-existing K-rich and Zn-rich phases in the K-Zn system to form an intermediate solid phase  $\text{KZn}_{13}$ .

thermally-induced transition

A transition that is induced by a change in temperature.

Example:  $\text{RbNO}_3$  undergoes three *structural transitions* below 573 K:

- (i) trigonal  $\rightarrow$  CsCl-type structure at 439 K,
- (ii) CsCl-type  $\rightarrow$  hexagonal structure at 501 K, and
- (iii) hexagonal structure  $\rightarrow$  NaCl-type structure at 551 K.

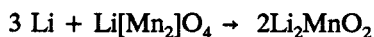
tie-line<sup>10</sup>

The line in a phase diagram joining the compositions of independent co-existing phases.

topochemical reaction<sup>25,26</sup>

A reversible or irreversible reaction that involves the introduction of a guest species into a host structure and that results in significant structural modifications to the host, for example, the breakage of bonds.

Example: The insertion of lithium at 50 °C into the spinel  $\text{Li}[\text{Mn}_2]\text{O}_4$  with symmetry  $\text{Fd}\bar{3}m$  to yield a layered structure with symmetry  $\text{P}\bar{3}m1$  <sup>41</sup>.



Alternative terms: *topotactic reaction*, *insertion reaction*.

topotactic reaction

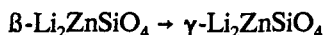
See *topochemical reaction*.



topotactic transition<sup>3,14,23</sup>

A transition in which the crystal lattice of the product phase shows one or more crystallographically equivalent, orientational-relationships to the crystal lattice of the parent phase.

Example: Transitions in which the anionic array is unchanged during the transition but cation reorganization occurs, as in:

triple point<sup>10</sup>

The point in a one-component system at which the temperature and pressure of three phases are in equilibrium. If there are  $p$  possible phases, there are  $p!/(p-3)!3!$  triple points.

Example: In the sulfur system four possible *triple points* (one metastable) exist for the four phases comprising rhombic S (solid), monoclinic S (solid), S (liquid) and S (vapor).

valence transition<sup>24</sup>

A transition observed in certain rare-earth and actinide materials in which the electronic occupation of the 4f or 5f orbital changes with external conditions for example, temperature and pressure.

Example: The transition at approximately 0.65 GPa where black, semiconducting  $\text{Sm}^{2+}\text{S}^{2-}$  changes to golden metallic  $(\text{Sm}^{3+} + e^+)\text{S}^{2-}$ .

Verwey transition<sup>3</sup>

An electron-ordering transition occurring in a mixed-valent system that results in an ordering of formal valence states in the low-temperature phase.

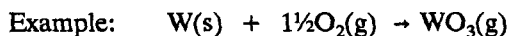
Example: The prototype system, first identified by Verwey, is the ferrosphenel magnetite,  $\text{Fe}^{3+}[\text{Fe}^{3+}\text{Fe}^{2+}]\text{O}_4$  in which an ordering of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions within octahedral sites is thought to occur below  $T_v \approx 120$  K.

virtual transition

A non-observable *liquid-crystal transition* that occurs below the crystallization temperature and is determined by extrapolation in binary phase diagrams.

volatilization<sup>8</sup>

The conversion of a solid or liquid to a gas or vapor by application of heat, by reducing pressure, by chemical reaction or by a combination of these processes.

**BIBLIOGRAPHY**

1. M B Bever (Ed.), *Encyclopedia of Materials Science and Engineering*, Pergamon Press, Oxford, 1986.
2. R Tottle, *An Encyclopedia of Metallurgy and Materials*, The Metals Society, Macdonald and Evans, Plymouth, 1984.
3. C N R Rao and K J Rao, *Phase Transitions in Solids*, McGraw Hill Inc., New York, 1978.
4. I Prigogine and R Defay (Translated by D H Everett), *Chemical Thermodynamics*, Longmans Green, London, 1954.
5. J S Rowlinson, *Liquids and Liquid Mixtures*, 2nd Edition, Butterworth, London, 1969.
6. J M Cowley, in *Modulated Structures - 1979*, AIP Conference Proceedings No. 53, American Institute of Physics, New York, 1979.
7. J E Ricci, *The Phase Rule and Heterogeneous Equilibrium*, Van Nostrand, Toronto/New York/London, 1951.
8. S P Parker (Ed), *Dictionary of Scientific and Technical Terms*, 3rd Edition, McGraw-Hill, New York, 1984.

9. R W Cahn (Ed.), *Physical Metallurgy*, 2nd revised Edition, North-Holland Publishing Company, Amsterdam, 1970.
10. A Prince, *Alloy Phase Equilibrium*, Elsevier, Amsterdam, 1966.
11. V Gold, K L Loening, A D McNaught and P Sehmi, in *Compendium of Chemical Technology: IUPAC Recommendations (The IUPAC "Gold Book")*, Blackwell Scientific Publications, Oxford, 1987.
12. M J Buerger, *Fortschr. Miner.* **38**(1), 9, 1961.
13. M J Buerger, *Soviet Physics - Crystallography* **16**(6), 959, 1972.
14. A R West, *Solid-State Chemistry and its Applications*, John Wiley and Sons, Chichester, 1984.
15. Rustum Roy, in *Phase Transitions - 1973*, H K Henisch, R Roy and L E Cross (Eds.), Pergamon Press, New York, 1973.
16. T C Collocott and A B Dobson (Eds.), *Dictionary of Science and Technology*, W & R Chambers Ltd., Richard Clay (The Chaucer Press) Ltd., Bungay, Suffolk, 1983.
17. C E Myers and R J Kematick, *J. Electrochem. Soc.*, **134**(3), 720, 1987.
18. J B Goodenough, *Magnetism and the Chemical Bond*, John Wiley, New York, 1963.
19. R E Newnham, *Structure-Property Relations*, Springer-Verlag, Berlin, 1975.
20. R G Lerner and G L Trigg (Eds.), *Encyclopedia of Physics*, 2nd Edition, VCH, New York, 1991.
21. J W Goodby, *J. Mater. Chem.*, **1**, 307, 1991.
22. K J Rao and C N R Rao, *J. Mater. Sci.*, **1**, 238, 1966.
23. A R West, *Z. Krist.* **141**, 422, 1975.
24. S P Parker (Ed.), *Encyclopedia of Science and Technology*, 6th Edition, McGraw-Hill, New York, 1987.
25. D W Murphy, *Advances in the Synthesis and Reactivity of Solids*, **1**, 237, 1991.
26. M S Whittingham and A J Jacobson (Eds.), *Intercalation Chemistry*, Academic Press, New York, 1982.
27. J Adams, in *Phase Transitions - 1973*, H K Henisch, R Roy and L E Cross (Eds.) Pergamon Press, New York, 1973.
28. G Meyrick and G W Powell, *Phase Transformations in Metals and Alloys*, *Ann. Rev. Mat. Sci.* **3**, 327, 1973.
29. S T Bowden, *The Phase Rule and Phase Relations*, Macmillan & Co., Ltd., London, 1945.
30. J B Goodenough, *Prog. Solid State Chem.*, **5**, 141, 1971.
31. R E Peierls, *Quantum Theory of Solids*, Oxford University Press, London, 1955.
32. D R Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd Edition, Hemisphere Publishing Corporation, New York, 1981.
33. C N R Rao, in *Solid State Chemistry*, C N R Rao (Ed.), Marcel Dekker Inc., New York, 1974.
34. J N Sherwood (Ed.), *The Plastically Crystalline State: Orientationally - Disordered Crystals*, John Wiley and Sons, Chichester, 1979.
35. J W Bray, L V Interrante, I S Jacobs and J C Bonner, in *Extended Linear Chain Compounds*, J S Miller (Ed.), Plenum Press, New York, Vol. 3, p. 353, 1983.
36. D R de Fontaine, *Clustering Effects in Solid Solutions* in *Treatise on Solid State Chemistry*, N B Hannay (Ed.), Vol. 5, Plenum Press, New York/London, 1975.
37. V Raghavan and M Cohen, *Solid-State Phase Transformations* in *Treatise on Solid State Chemistry*, N B Hannay (Ed.), Vol. 5, Plenum Press, New York/London, 1975.
38. C M Wayman, *Solid-State Phase Transformations*, *Ann. Rev. Mat. Sci.*, **1**, 185, 1971.
39. S C Abrahams, in *Phase Transitions - 1973*, H K Henisch, R Roy and L E Cross (Eds.), Pergamon Press, New York, 1973.
40. R W G Wyckoff, *Crystal Structures* (Second Edition), John Wiley & Sons, London, 1963.
41. W I F David, J B Goodenough, M M Thackeray and M G S R Thomas, *Rev. de Chim. Miner.*, **20**, 636, 1983.