Structural Phase Transitions I

Edited by K.A. Müller and H.Thomas

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With Contributions by
B. Dorner P.A. Fleury B. Lüthi K. Lyons
K.A. Müller W. Rehwald

With 61 Figures

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Professor Dr. K. Alex Müller
IBM, Zürich Research Laboratory, CH-8803 Rüschlikon, Switzerland

Professor Dr. Harry Thomas
Institut für Physik, Universität Basel, CH-4056 Basel, Switzerland

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Preface

The growth and maturity of research in structural phase transitions (SPT) make it an appropriate subject for the Topics in Current Physics series. The maturing process is, however, by no means complete. New areas such as incommensurable SPT, quasi-low-dimensional systems, systems containing lattice disorder due to impurities or as mixed crystals, multicritical points, and quantum effects have recently come under focus. The understanding of the dynamics, be it microscopic soft-mode theory or critical dynamics, more specifically the central-peak problem, is also still quite incomplete. On the other hand, there are areas which are genuinely consolidated. On the theoretical side, these concern symmetry properties, Landau theory, and the application of static renormalization theory to critical phenomena. Also, the use of various complementary experimental techniques, with their specific merits, are well in hand.

The field of STP's and of the various methods of investigation range so widely that it appeared appropriate to invite a number of scientists to review their respective areas of expertise to which they have made significant contributions. Therefore, the style and taste in the different chapters will, of course, vary to some extent. This diversity, however, guarantees a penetration of each area, in width and depth, to a degree which would have been difficult to achieve with a single author or through a small team covering the whole field. For instance, there are very few experimentalists who can cover scattering techniques as well as magnetic resonance methods with a comparable degree of competence, although important contributions to the field have been obtained by both techniques.

This volume is the first of an intended total of three. In the Introduction following this Preface the more general aspects of our content will be emphasized. This volume contains three chapters on experimental research. The contribution by Lyons and Fleury (Chap.2) discusses optical investigations, particularly light scattering, followed by an extensive bibliography. Then, Dorner reviews the results achieved by inelastic neutron scattering (Chap.3). He, together with Comes, has already presented certain aspects of this area, especially of a technical nature, in an earlier article in Topics in Current Physics (Vol.3). The new chapter emphasizes results not touched upon in the previous one. Chapter 4 by Lüthi and Rehwald gives an up-to-date account of the ultrasonic work. Another experimental volume is planned to consist again of three chapters, including results achieved with the remaining experimental techniques used in SPT, electron-paramagnetic and nuclear magnetic resonance, dielectric measurements, and caloric techniques. The theoretical volume will start with dynamic lattice theory, then go on to the Landau theory, general symmetry properties, and renormalization group theory, and end with a special chapter on the Jahn-Teller induced SPT.

It is the hope of the undersigned that the efforts made may serve their purpose, to help as an introduction into the various area of research in SPT, give a valid description of the state of the art as well as its possible future lines of research, and to serve as a reference.

Zürich, Basel, October, 1980 *K.A. Müller. H. Thomas*

Contents

1. Introduction

K. A. Müller

With 2 Figures

The areas of research on structural phase transitions (SPT) enumerated in the Preface give a general impression of the field of interest addressed in this series. Here we want to provide a wider perspective. The change of structure at a phase transition in a solid can occur in two quite distinct ways. First of all, those transitions where the atoms of a solid *reconstruct* a new lattice, for example, when graphite transforms into diamond or if an amorphous solid changes to the crystalline state. Secondly, there are those where a regular lattice is *distorted* slightly "without in any other way disrupting the linkage of the net" according to BUERGER [1.1]. This can occur as a result of small *displacements* in the lattice position of single atoms or molecular units on the one hand or the *ordering* of atoms or molecules among various equivalent positions on the other hand. Due to the matter transport, which is inherently involved in reconstructive transitions, they are often slow (recrystallization). Because they are transitions which are not symmetry related in any way they have to be of first order. Reconstructive transitions are not considered in the following chapters. It is only the second category, above, to which this series is devoted. Therefore SPT are understood throughout in this narrower sense, introduced a decade ago [1.3] and used widely since then by solid-state physicists but not among crystallographers [1.2]. Martensitic phase transformations are also somewhat outside the present scope and are addressed only in Chap.4.

In the study of phase transitions the order parameter $\eta(T)$ is a crucial quantity. Below the transformation T_c it is nonzero and increases on cooling. In a ferromagnet it is the mangetization $M(T) = V^{-1} \sum_i (\mu^i_{0+} - \mu^i_{0-})$ which measures the number of ordered atomic magnetic moments μ_0, per unit volume, of an infinite solid, in the magnetization direction. This corresponds to the order parameter $Q(T) = V^{-1} \sum_i (Q^i_{0+} - Q^i_{0-})$ in a pure order-disorder SPT. A distinction between the latter and a displacive transition is possible on the basis of atomic single cell potentials [1.4]. This is shown in Fig.1.1, schematically for one spatial coordinate Q: with anharmonic potential $V(Q) = aQ^2 + bQ^4$ with constants $a < 0$ and $b > 0$. This double well potential has two minima and a maximum, their difference ΔE being $\Delta E = a^2/4b$. If the depth of the two energy wells $\Delta E \gg kT_c$ the transition occurs due to ordering between $Q^i_{0\pm} = \pm\sqrt{-a/2b}$. On the other hand, if $\Delta E \ll kT_c$ a *continuous* cooperative displacement of atoms along Q below T_c is found as a function of temperature, at least in mean field theory [1.5].

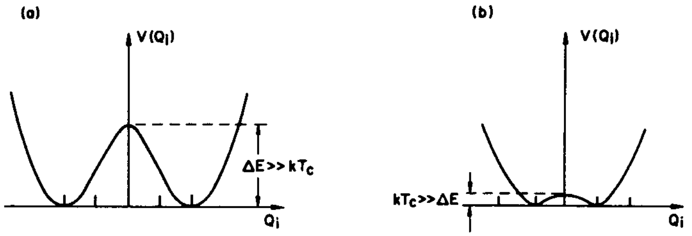

Fig. 1.1. Single cell potentials in (a) order-disorder (b) displacive SPT system

The transitions themselves result from the coupling of different cells, i and j, in the regular lattice; there is an interaction energy $V = \sum_{i>j} c_{ij}Q_iQ_j$. A nonzero single cell anharmonicity is, however, also needed in displacive systems. A completely harmonic potential, i.e., a parabolic single cell potential, does not yield a phase transition despite $V \neq 0$.

Using self-consistent mean field theory one derives the free energy of the system to be [1.5]

$$F = F_0 + A\langle Q\rangle^2 + B\langle Q\rangle^4 + \text{higher order} , \qquad (1.1)$$

where F_0 contains all other degrees of freedom of the system, $\langle Q\rangle = Q(T)$, $A = \alpha(T - T_c)$ and α and B can be viewed as nearly temperature independent, near T_c. Equation (1.1) is the expression Landau found from group theoretical arguments in 1937, assuming that the space group of the low-temperature phase is a subgroup of its high symmetry parent or prototype phase [1.6], and no third-order invariant exists. Furthermore, the order parameter Q(T) is a scalar; it has but one dimension. We shall come back to the fundamental importance of the Landau free energy expansion for the more general cases in SPT, as well as its modern Hamiltonian version in renormalization group theory.

Upon minimization of (1.1) with respect to $\langle Q\rangle$, one finds a second-order transition at T_c when $B > 0$ with a continuous order parameter varying as $\langle Q\rangle^2 \propto (T_c - T)$ (see Fig.1.2). If symmetry allows a third-order invariant $C\langle Q\rangle^3$ in (1.1), a first-order transition at $T_0 > T_c$ results with a discontinuous jump of the order parameter [1.7]. The transition is then sometimes called "weak" first order not only because the jump in $\langle Q\rangle$ can be quite small, but because the low-temperature phase is still a subgroup of the high-temperature one. On the other hand, for the reconstructive transitions mentioned at the beginning, no such symmetry relation exists. The transition occurs, in that case, when the high and low symmetry free enthalpies equal each other, and there can be considerable metastability.

The dynamic behavior of the two types of distortive SPT is also quite different. The order-disorder systems behave like the magnetic ones. Above T_c their excitation

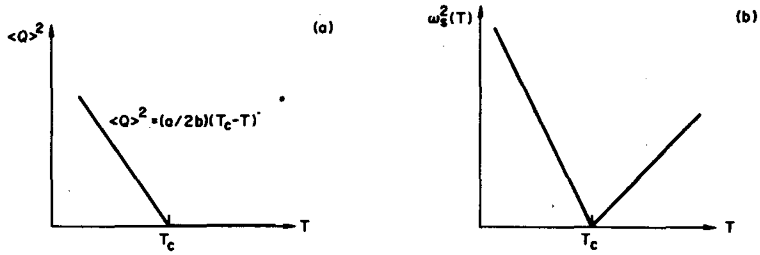

Fig. 1.2. (b) $\omega_s^2 = 2(a/m)(T-T_c)$ for $T>T_c$; $\omega_s^2 = 4(a/m)(T_c-T)$ for $T<T_c$

spectrum shows relaxational character and is centered around $\omega = 0$. Only below T_c do we find a mode at finite frequency $\omega \neq 0$ (as for spin waves in ferromagnets). On the other hand, in displacive systems, a mode of finite frequency exists even above T_c, and tends to freeze out on approaching T_c from above. It is obtained from (1.1) by solving the dynamical matrix [1.5]

$$\partial^2 F/\partial\langle Q\rangle^2 = m\omega_s^2(T) , \qquad (1.2)$$

taking into account the inertia of the atoms.

This soft mode $\omega_s(T)$ was a concept introduced two decades ago first by COCHRAN [1.8,9] and was extremely fruitful both for experimental and theoretical research in SPT. Table 1.1 lists the SPT systems and their soft mode character. As ferroelectric examples we cite $BaTiO_3$ which is more of the displacive, and KH_2PO_4 which is more of the order-disorder variety, although it is now recognized that they are by no means "pure" examples. Using the terms of Fig. 1.1, ΔE is of the order of kT_c in both cases, in one somewhat larger and in the other slightly smaller. The soft-mode concept has been extended to pure order-disorder relaxational systems [1.10], where in a mean field approximation $2\pi/\tau = \omega_r \propto (T-T_c)$, whereas $\omega_s \propto (T-T_c)^{\frac{1}{2}}$ (see Fig.1.2). However, if the soft phonon is overdamped its temperature dependence cannot be distinguished from a relaxational response [1.11]. The Jahn-Teller systems listed in Table 1.1 also deserve comment. These phase transitions come about through the coupling of electronic and acoustic degrees of freedom. The former can be localized like the 4f electrons in $TbVO_4$, or else delocalized as in Nb_3Sn, in which case they are called band JT transitions.

The modes of a lattice, or their quantized equivalent, the phonons, are probed most directly by inelastic scattering of photons or neutrons. Chapter 2 in the present volume is devoted mainly to the first of these techniques, light scattering, and Chap.3 is devoted entirely to neutron scattering. Fleury and Lyons give characteristic examples of the various SPT systems in each section of their chapter. Their choices, for particular substances, differ in part from the list in Table 1.1. (If the light is scattered by optical modes it is called Raman scattering whereas

Table 1.1. SPT systems and their soft modes

short range forces	($SrTiO_3$)	optic (xy)
dipolar, ferroelectric	($BaTiO_3$)	t. optic (x)
	(KH_2PO_4)	t. optic/t. acoustic
ferroelastic	(TcO_2)	acoustic
Jahn-Teller, ion	($TbVO_4$)	electronic/acoustic
band	(Nb_3Sn)	
charge density wave	($NbSe_2$)	electronic/acoustic

that scattered from acoustic modes is termed Brillouin scattering [1.7].) Their chapter gives the reader an understanding of the different SPT types and also of characteristic differences between possible soft modes. Furthermore, examples of Brillouin center, boundary, and incommensurate soft modes are reviewed (we shall define these terms below). Their latter section is a valuable introduction to this type of SPT.

The modes of a crystal, characterized by a dispersion relationship $\omega(\underline{q})$, of a crystal, are collective excitations and extend over the whole wave vector space $\underline{q}$ of the Brillouin zone. At a displacive transition the freezing out of the soft mode produces the lattice found on the low-temperature side of the transition. For $T > T_c$, $\omega_s(\underline{q})$ has a minimum at some wave vector in $\underline{q}$ space. This minimum is most often found at the zone center $\underline{q} = 0$ or at particular points of the Brillouin zone boundary $\underline{q}_b$. Accordingly they are termed *zone center* and *zone boundary transitions* in Chap. 2. In the latter case the unit cell gets doubled (or subject to even higher multiplication) in the low-temperature phase because the point $\underline{q}_b$ gets "folded into" the zone center. (The soft mode unit vector in the low-temperature phase transforms as the identity representation of the space group). Denoting the unit cell volumes by z^h and z^ℓ, respectively, one can describe the situation statically by

$$z^\ell = nz^h \quad (1.3)$$

with n = 1 and n = 2r (r integer) in the two cases. These cases have been termed *ferro* and *antiferrodistortive* by GRÄNICHER and MÜLLER [1.12] earlier. In certain crystals molecular units order, as does NH_4 in NH_4Cl, below the cubic-cubic ordering phase transformation. Because no distortion occurs at T_c, the transition is called *ferro-order* (see Chap.3 for a discussion). The corresponding antiferro order in NH_4Br is equivalent to antiferrodistortive as the unit cell is doubled and distorted. As long as n in (1.3) is a rational number $n = r_\alpha/r_\beta$ with integral r_i and $r_\alpha > r_\beta$, the corresponding wave vector $\underline{q}$ of $\omega_s(\underline{q})$, inside the zone, is a rational multiple of a particular Brillouin zone boundary wave vector $\underline{q}_b$. The transition is then called *commensurate*. If however n is an irrational number the transitions are called *incommensurate* [1.13]. Some of the most recent studies in SPT are aimed towards an understanding of this interesting class of incommensurate transitions.

Up to now one may think that the descriptions of SPTs in terms of free energy or of soft modes are equivalent. We want to point out here that the free energy discussion is more general for the following reasons: First, if a transition has essentially reorientational and/or relaxational character, as does $NaNO_2$ where electric NO_2 dipoles reorient and order ferroelectrically, many solid-state physicists are reluctant to name this a zone center mode transition. The above-mentioned NH_4Cl is another example. A more important and second reason: There are continuous transitions where no microscopic dynamical fluctuations, i.e., soft or relaxational modes of finite wave vector, are present. A crystal has, in general, 6 independent elastic degrees of freedom, but only 3 acoustic modes. If one of these acoustic modes is soft, the transition is a ferroelastic SPT (see Table 1.1). However, one of the other 3 independent elastic degrees, not related to the acoustic modes, may become critical: then a ferroelastic transition occurs but no acoustic mode becomes soft. It is just an isolated point at the zone center whose elastic constant shows temperature dependence. Then the crystal free energy is given exactly by (1.1). Such a "type zero" SPT occurs generally for symmetry nonbreaking transitions and has most recently been observed in KH_2PO_4, in the presence of an electric field [1.14].

The wavelength of light is of a few thousand Å; this limits the wave vector scattering range of phonons essentially to the center of the Brillouin zone. On the other hand, the wavelength of thermal neutrons is of the order of Angstroms and their energy matches that of phonons [1.7]. This allows probing over the entire Brillouin zone. In Chap.3, Dorner first recalls the general aspects of inelastic neutron scattering near SPT and soft mode analysis. He then goes on to review some of the classic work on displacive SPT. His next section is devoted to the observation of central peaks, i.e., critically enhanced excitations near $\omega = 0$, observed for temperatures T above T_c, first reported in $SrTiO_3$ [1.15], and distinct from the underdamped soft phonons, and thus not contained in the classical picture. The narrowness of the observed features clearly points to the involvement of impurities in the dynamics, but not necessarily to the critical enhancement of the central peak, as well as the nonfreezing out of the soft mode [1.16]. Other central peaks seen for $T \leq T_c$ have been probed by light scattering and are reviewed in Chap.2. Both accounts bring in touch with the recent as yet in part unsolved problems as to the origin of these excitations.

Subsequently Dorner introduces and describes studies in molecular crystals and the occurring SPT. This is the first summary, in the literature, of the field. The importance of the incoherent structure factor for the determination of molecular reorientation rates is emphasized. Then, examples of the librational dynamics of molecules, and of their various degrees of coupling to the translational modes, if any, are given. The ensuing molecular cluster formation near T_c is discussed. The concise nature of the account also makes it useful for experts in SPT. Dorner's last section is devoted to incommensurable SPT. It is the first account of inelastic scattering results and can be recommended as an introduction as well as an update to what has been achieved in charge density wave systems as well as in insulators or more exotic quasi-one-dimensional chain systems.

The soft modes can couple to other modes in the lattice. If the soft mode is an optical one it can couple to acoustic modes. Thus Brillouin scattering from the latter can monitor the soft mode temperature dependence, damping, etc. Theoretical aspects of coupling are discussed in Chap.2. However, one can probe the acoustic mode directly with ultrasonic dispersion and absorption measurements. In Chap.4 Lüthi and Rehwald review in depth the work done with this technique. It is, in favorable cases, one of the most accurate in the entire field. The authors give a clear account of the theoretical analysis. Depending upon whether the strain in the crystal couples linearly, or through higher order, to the order parameter, the ultrasound behavior as a function of temperature can be quite different. In the first case the strain itself can be taken as the order parameter and an elastic constant vanishes at a second-order phase transition. Thoroughly explored examples of the ferroelectric-ferroelastic as well as the two Jahn-Teller varieties (see Table 1.1) are presented. This is followed by a review of those cases where the order parameter couples quadratically to strain, and a critical reduction of an elastic constant with enhanced ultrasound attenuation is observed, near T_c. They can be used to determine phase diagrams as a function of an external applied parameter. In short, their review covers all systems shown in Table 1.1, and also mixed valence systems and martensitic transitions, not discussed elsewhere in this series.

An SPT can be monitored by the local displacements of the constituents of the lattice. X-rays and elastic neutron scattering have long been standard techniques for such investigations. Results of this sort can be found in a number of works. We should like to mention here the well-balanced Chap.5 in MEGAW's book on crystal structures [1.2]. In the context of this series the understanding and use of space groups is obviously of importance; their relatively infrequent use may be traced to the fact that no good introductory text was available for solid-state physicists. This gap in the literature has now been filled with the indeed readable book by BURNS and GLASER [1.17]. Knowledge of group theory and space groups will, in part, be required to fully appreciate the two chapters in the theoretical volume on Landau theory and general symmetry properties.

There exist now a number of recent techniques for probing the existence, amount, and symmetry of local displacements in a solid. These are in part one to two orders of magnitude more sensitive than the older ones. Optical fluorescence is one technique which is reviewed in Chap.2. Electron and nuclear magnetic resonances (EPR and NMR) as well as the Mössbauer effect are others. The first is very sensitive to static displacements and will be presented in the second volume, as will NMR.

The latter is less sensitive but certainly probes the bulk of the crystal. It gives useful information about the local atomic or molecular time-dependent motion. Using these sensitive techniques, as well as ultrasound dispersion and absorption, it is now firmly established that the static and dynamic behavior near SPT which results from short range interactions, differs from the one predicted by Landau and soft mode theory in the absence of impurity effects. Furthermore, on application of external forces, such as uniaxial stress or hydrostatic pressure, multicritical points are observed in which two or more second-order phase boundaries join as the external fields are varied. An example is the bicritical point in $SrTiO_3$ mentioned in Chap.4. In this very active field renormalization group theory has predicted certain topologies which are universal and depend only on the symmetry of the lattice, its dimensionality, and that of the order parameter. Some were first verified in SPT, rather than in the "competing" field of magnetic transitions. Such findings and a chapter on dielectric and caloric methods are planned to be the content of the follow-on volume.

The various experimental techniques employed in SPT research are often complementary. Depending on the information wanted in a particular case and the samples available, one method may yield more accurate or valuable information than another. Often the availability of samples or their gross macroscopic properties may inhibit their investigation with a certain technique. For example, if the crystal is large, buth highly conducting, ultrasound measurements are easily performed but it is difficult to use paramagnetic resonance, because the microwaves cannot penetrate the sample. On the other hand, if the available crystals are very small but nonconducting EPR or light scattering can be well employed, whereas classical ultrasound absorption methods are excluded due to phase and amplitude inhomogeneities in the small sample. The new phonon echo method may become useful here in the future [1.18]. Small crystals also create difficulty for inelastic neutron scattering, even in high flux reactors, especially if atoms with small scattering cross section have to be probed.

The above examples show that an assessment of experimental methods is in order. This has been done in each of the chapters. The descriptions of the techniques are concise and to the point, but fairly complete in Chaps.2 and 4. In view of the fact that the classical inelastic neutron scattering techniques have already been described in [1.11], they have not been repeated in Chap.3. This gave space for a review of the most recent developments of high-resolution instruments.

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References

1.1 M.J. Buerger: In *Phase Transitions in Solids* (Wiley, New York 1951) p.133
1.2 H.D. Megaw: *Crystal Structures, A Working Approach* (W.B. Saunders, Philadelphia 1973)
1.3 K.A. Müller, W. Berlinger, F. Waldner: Phys. Rev. Lett. *21*, 814 (1968)
1.4 A.D. Bruce: In *Solitons and Condensed Matter Physics*, Springer Series in Solid-State Sciences, Vol. 8, ed. by A.R. Bishop, T. Schneider (Springer, Berlin, Heidelberg, New York 1978) p. 116
1.5 H. Thomas: In *Structural Phase Transitions and Soft Modes*, Proceedings of the Nato Advanced Study Institute, ed. by E.J. Samuelsen, E. Andersen, J. Feder (Universitetsforlaget, Oslo 1971)
1.6 L. Landau, E. Lifschitz: *Physique Statistique* (MIR, Moscow 1967)
1.7 C. Kittel: *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York 1965)
1.8 W. Cochran: Phys. Rev. Lett. *3*, 412 (1959)
1.9 P.W. Anderson: In *Fizika dielektrikov*, ed. by G.I. Skanavi (Acad. Nauk, SSR, Moscow 1960) p. 290
1.10 R. Blinc, B. Zeks: In *Soft Modes in Ferroelectrics and Antiferroelectrics*, ed. by E. P. Wohlfarth (North-Holland, Amsterdam 1979)
1.11 B. Dorner, R. Comes: In *Dynamics of Solids and Liquids by Neutron Scattering*, ed. by S.W. Lovesey, T. Springer, Topics in Current Physics, Vol.3 (Springer, Berlin, Heidelberg, New York 1977) p.127
1.12 H. Gränicher, K.A. Müller: Mater. Res. Bull. *6*, 977 (1971)
1.13 A. Janner, T. Janssen: Phys. Rev. B*15*, 643 (1977)
1.14 E. Courtens, R. Gammon, S. Alexander: Phys. Rev. Lett. *43*, 1026 (1979)
1.15 T. Riste, E.J. Samuelsen, K. Otnes, J. Feder: Solid State Comm. *9*, 1455 (1971)
1.16 K.A. Müller: In *Dynamical Critical Phenomena and Related Topics*, Lecture Notes in Physics, Vol. 104, ed. by C.P. Enz (Springer, Berlin, Heidelberg, New York (1979) p. 210
1.17 G. Burns, A.M. Glazer: *Space Groups for Solid State Scientists* (Academic Press, New York 1978)
1.18 N.S. Shiren, R.L. Melcher: In *Phonon Scattering in Solids*, ed. by L.G. Hallis, W.U. Rampton, A.F.G. What (Plenum, New York 1976) p. 405

2. Optical Studies of Structural Phase Transitions

P. A. Fleury and K. Lyons

With 26 Figures

A review is presented of the application of optical techniques to the study of structural phase transitions. The techniques discussed include static measurements (refractive index, birefringence) as well as those providing dynamic information (light scattering, IR and optical absorption, fluorescence). The use of nonlinear optical techniques such as second harmonic generation is also discussed. In a background section, the various experimental techniques are delineated with descriptions of the relevant apparatus and theoretical considerations, including comparison to the information available from other techniques. The various classes of phase transitions are then discussed in turn, organized according to the symmetry and periodicity of the order parameter. Emphasis is on the developments of the last few years, including optical studies of central peak and mode coupling phenomena, and recent developments in the use of Fourier transform spectroscopy. An extensive bibliography on this very broad subject is included as an adjunct to the review, categorized by the type of phase transition and by the experimental technique involved.

2.1 Background

The recent rapid growth of the field of optical research, triggered by the advent of the laser, has been accompanied, not accidentally, by a comparable revolution in our understanding of phase transitions [2.1-3]. In this review we are concerned with the ways in which optical techniques have contributed to this understanding. There is a vast literature in this field, even within the last few years, and it would be impossible in the space of this review to describe it all in any reasonable detail. Therefore, we have decided to limit the discussion in several ways. We have chosen to exclude all work on plastic crystals. In addition, since most magnetic transitions do not involve structural changes and there have been two very recent review articles on optical investigation of magnetic crystals [2.4,5], we shall exclude these also from consideration. Finally, we have decided to present only certain specific examples in detail. This means that much of the literature is not referenced directly in the text. Thus, at the end of this review we include a categorized bibliography, representing the results of an extensive literature search. We feel that this organization best serves the purpose for which this review is intended.