THERMAL TRANSFORMATIONS IN SOLIDS

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Introduction

The Inadequacy of Classical Phase Relations for describing Transitions between Condensed Phases.—The classical approach to the phase rule was based on the concept of independent phases in equilibrium. On this basis, separate equations of state can be attributed to each phase, the properties of which can be summarised in the molar free energy functions. For the purposes of this Review, which is concerned primarily with one-component systems, the free-energy function G takes the form $G = \mathrm{f}(p, T)$ where p, T are chosen as independent variables. This is the equation of a surface. When two independent phases are in equilibrium their molar free energies are equal so that transitions between phases are located thermodynamically on the intersections between surfaces. Much of the classical discussion of phase transitions was presented in terms of geometrical conclusions about the intersections between independent free-energy surfaces.[1a] It is convenient to consider sections of these surfaces by the planes $p =$ constant and $T =$ constant. Of particular importance are the derivatives

$$\left(\frac{\partial G}{\partial T}\right)_p = -S\,; \quad \left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right) = -\left(\frac{\partial S}{\partial T}\right)_p = \frac{-C_p}{T}\,; \quad \left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T = -\chi V$$

$$\left(\frac{\partial^2 G}{\partial p . \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_p = \alpha V$$

since these refer to readily observable experimental quantities such as the entropy S, the molar volume V, the specific heat C_p, the isothermal compressibility χ, and the thermal expansion α. According to the classical geometrical concepts of a transition between two independent phases, 1 and 2, the G curves intersect at a sharp angle, and the differences between the slopes of the tangents

$$\left(\frac{\partial G_1}{\partial T}\right)_p - \left(\frac{\partial G_2}{\partial T}\right)_p = S_2 - S_1 = +\Delta S \quad . \quad . \quad . \quad (1A)$$

$$\left(\frac{\partial G_2}{\partial p}\right)_T - \left(\frac{\partial G_1}{\partial p}\right)_T = V_2 - V_1 = \Delta V \quad . \quad . \quad . \quad (1B)$$

represent the change in molar entropy and in molar volume respectively.

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[1] (*a*) See Findlay, " The Phase Rule and its Applications ", Longmans, Green, London, 1938, 8th edn., and earlier textbooks ; (*b*) Lumsden, " Thermodynamics of Alloys ", Monograph, Institute of Metals, London, 1952.

These are interrelated by the classical Clausius–Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as proved in standard textbooks of thermodynamics.

Various lines of inquiry have led to the conclusion that for certain transitions between phases the classical phase relations are inadequate.[2] This is particularly evident for transitions between condensed phases, such as solid–solid, solid–liquid, and anisotropic liquid–isotropic liquid, though it also applies to some extent around the critical temperature for liquid–vapour transitions. Well away from the critical temperature, the classical phase rule can still be applied for solid–vapour and liquid–vapour transitions. Though some of what follows also applies in modified form to transitions involving liquids[3] this Review deals specifically only with solid–solid transformations.

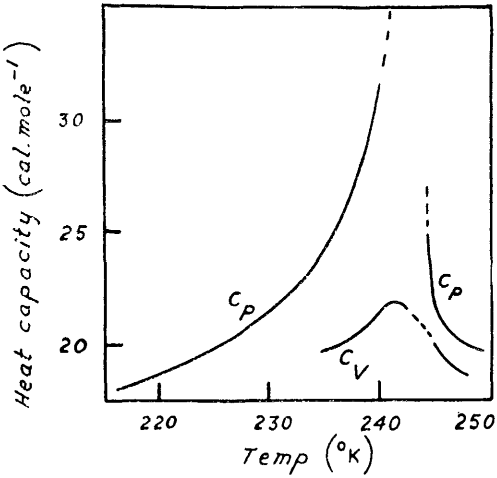

Fig. 1

Heat capacity of ammonium chloride.

[Reproduced from Ubbelohde, " Modern Thermodynamical Principles ", Oxford Univ. Press, 1952, p. 81.]

The most direct thermodynamic evidence about the inadequacy of the classical phase rule in describing certain transformations in solids arises from experimental measurements of specific heats and specific volumes. For example, many ammonium salts (see p. 269) show a marked anomaly in the specific heats, which rise to a peak value around − 31° C and fall back at still higher temperatures to values more characteristic of normal crystal lattices.

The fancied resemblance of such curves to the Greek capital letter Λ (lambda) has led to the description of such phenomena as " lambda-point anomalies ". Measurements of specific volumes show a corresponding

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[2] Ubbelohde, *Brit. J. Appl. Phys.*, 1956, **7**, 313.

[3] *Idem, Quart. Rev.*, 1950, **4**, 356.

anomalous increase spread over a temperature interval, so that coefficients of thermal expansion also pass through a peak before returning to more normal values.

This kind of behaviour, which is now known in many classes of crystal, obviously suggests that the classical abrupt change in heat content or specific volume at a transition point, which corresponds with a discontinuous change in tangent slopes to the two free-energy curves, has in some way been spread over a narrow range of temperatures. Contrary to the hypothesis of wholly independent phases, actual observations show that the free energy of the low-temperature structure 1 exhibits to varying degrees a " forewarning " of the transformation, which likewise modifies the trend of free energy of structure 2 near a transformation. For various geometrical aspects of " forewarning ", which will not be detailed here, see refs. 3 and 4.

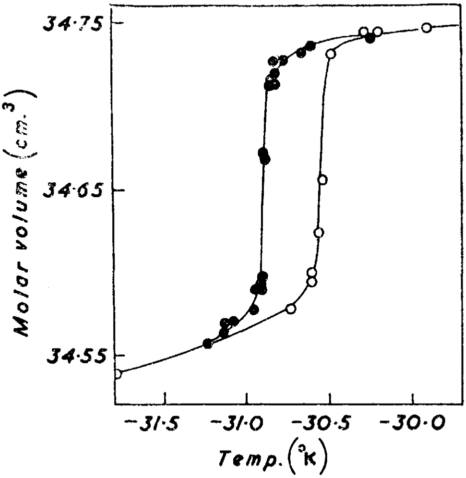

FIG. 2

Molar volume for sublimed crystals of ammonium chloride.

A second fundamental criticism about the application of the classical phase rule to solids arises from the consideration that when a change of structure has occurred in a solid, contributions from strain energy ξ or internal surface energy η to a certain extent play the part of additional degrees of freedom in the free-energy equations. When these terms are important in equations such as

$$G = \mathrm{f}(p, T, \xi, \eta) . \quad . \quad . \quad . \quad . \quad (3)$$

a modified phase rule [5] has to be applied

$$F = (C + 2) + \Sigma\pi - P \quad . \quad . \quad . \quad . \quad (4)$$

where $\Sigma\pi$ refers to the additional " degrees of freedom " introduced. These

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[4] Jaffray, *Ann. Physique*, 1948, **3**, 5.

[5] Ubbelohde, *Proc. Roy. Soc.*, 1937, *A*, **159**, 301.

are particularly important in the phenomenon of hysteresis discussed later, which modifies the conventional significance attributed to a " degree of freedom ".

Mathematical Theories of Phase Transformations of " Higher Order ".—Early attempts to interpret " smeared or diffuse transitions " followed the classical approach of the phase rule in being fundamentally mathematical theories that pay no regard to the *structural* changes taking place. It was pointed out by Ehrenfest[6] that if two free-energy curves made contact, this corresponded mathematically with an intersection of higher order. Standard mathematical theory about curves shows that intersections of the second or third order correspond with contact of the first or second order respectively. When intersections between curves are of order higher than unity, one mathematical consequence is that, instead of a discontinuity in the first derivatives of the G functions as in equations ($1A$ and $1B$), discontinuities are only found in the second, or third, or higher derivatives, according to the order of intersection encountered.

The most important mathematical outcome of this theory is that the Clausius–Clapeyron equation (2) which applies for discontinuous transitions of the first order must be replaced by equations involving differentials of higher order. The precise form these take depends on assumptions about the " order " of contact, which may not be realistic structurally (see p. 261). For example, Ehrenfest derives the relations

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\alpha_2 - \alpha_1}{\chi_2 - \chi_1} = \frac{C_2 - C_1}{TV(\alpha_2 - \alpha_1)}$$

where α is the thermal expansion, χ is the compressibility, and C the specific heat at constant pressure. For more detailed discussions about these and other relations for continuous transitions see refs. 6 and 7.

Ehrenfest's theory is not quite satisfactory even from a purely formal standpoint, since in an intersection of the second order the G curves for " phase " 2 lie wholly below those of " phase " 1 throughout the diagram (as in Fig. 3, *b*) so that 1 would never be stable relative to 2. This formal difficulty was obviated by Justi and von Laue[8] who suggested that lambda-point transitions were in fact of the third order so that crossing as well as contact of the G_1 and G_2 curves was implied, as in Fig. 3, *a*.

In order not to prejudice interpretation, transformations which behave experimentally broadly in accordance with classical thermodynamics will be termed *discontinuous* in what follows. Even discontinuous transformations may show forewarning to a varying extent (see p. 248). Transformations which show no classical discontinuity are described as *continuous*. Where there is evidence that " continuity " arises through a coexistence of two distinct structures over a narrow range of temperature in a hybrid single crystal, in ways more fully discussed below, such " continuous "

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[6] Ehrenfest, *Proc. Amsterdam Akad.*, 1933, **36**, 153.

[7] (Symposia) (*a*) " Phase Transformations in Solids ", Wiley, New York, 1951 ; (*b*) " Changements de Phase ", Société de Chimie physique, Paris, 1952.

[8] Justi and von Laue, *Z. tech. Phys.*, 1934, **15**, 521 ; *Phys. Z.*, 1934, **35**, 945.

transformations are best described as " smeared " transformations from one structure into another. This terminology [9] is further discussed later.

In spite of its great influence on the development of research in thermal transitions, the mathematical theory of Ehrenfest and of Justi and von Laue has serious defects. These arise from their complete disregard of important features of crystal structure and crystal behaviour, which may be briefly summarised as follows :

(i) Studies of crystal structure have shown that whenever a continuous transformation is found, any change of structure above and below the transformation is only small. This fact is not in contradiction with the mathematical theories, but its full significance only emerges when all the structural aspects of continuous transformations are considered.

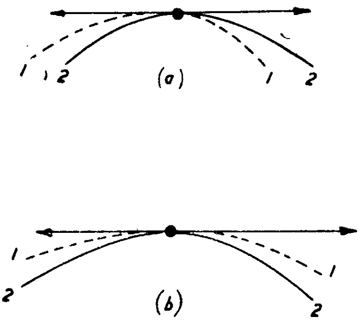

FIG. 3

(ii) It is very important to determine whether apparent continuity of transformation only arises when the properties of polycrystalline samples are studied, or whether continuity is also found in the properties of single crystals taken through a transformation cycle. This distinction is irrelevant in the classical phase rule in which a " solid " was assumed to be in " equilibrium " at every stage of the transformation. Actually, however, it is of great significance in " smeared " transformations, where the averaging of behaviour in a polycrystalline sample may simulate a smoothness of change which need not apply to individual single crystals.

(iii) Consideration of the structural aspects of a transformation brings out the importance of hysteresis, which is often associated with continuous transformations. Hysteresis can be an essential part of a smeared transformation when this takes place by way of hybrid single crystals, in which two closely similar structures coexist over a narrow range of temperature.

Crystal structure and thermodynamics of transformations in solids.

Discontinuous Transformations.—At 0° K the crystal structure with the lowest lattice potential energy has the highest stability. Subject to the limitations indicated by valency theory, more than one type of crystal

[9] Cf. Ubbelohde and Woodward, *Nature*, 1945, **155,** 170 ; 1945, **156,** 20 ; *Proc. Roy. Soc.*, 1946, *A*, **185,** 448 ; 1947, *A*, **188,** 357.

lattice can often be formulated, for example, for ionic crystals or for metals. But the difference of lattice energy between such structures is usually quite large, so that there is no difficulty in predicting which form will be stable at 0° K and zero pressure. Crystals whose force fields are primarily determined by van der Waals forces and hydrogen bonds frequently exhibit a diversity of structures with about the same lattice energy, since the various forces are all of the same order.

Under increased pressures the changing contribution of repulsion forces to the lattice energy is often quite different for different crystal polymorphs ; transitions are theoretically possible at 0° K for this reason. Effects of increased pressure on crystal transformations will not be discussed in detail in this Review.[10]

At ordinary pressures, when there is a comparatively large difference of lattice structure between two polymorphic forms of a substance, the existence of a transformation temperature above 0° K arises when the two polymorphs have sufficiently different rates of increase of entropy with temperature. Formally the conditions required are $[G_1]_0 - [G_2]_0 < 0$; 1 stable at 0° K ; and $\mathrm{d}G_1/\mathrm{d}T > \mathrm{d}G_2/\mathrm{d}T$. These conditions permit a transformation temperature T_c such that

$$[G_1]_0 + \int_0^{T_c} \mathrm{d}G_1 = [G_2]_0 + \int_0^{T_c} \mathrm{d}G_2$$

In changes of G with temperature the difference in heat content between two polymorphs usually does not change much with temperature. The main factor leading to transformation is the increasing divergence of crystal entropies. One highly important origin of entropy differences between polymorphs, leading to a thermal transition, arises from vibrational entropy. Alternative crystal forms of the same substance all have zero entropy at 0° K if they obey the Nernst heat theorem, as may usually be assumed in the absence of special evidence to the contrary. At higher temperatures, the entropy difference

$$S_2 - S_1 = \int_0^{T_c} (C_{p_2} - C_{p_1})\mathrm{d}\ln T$$

eventually compensates for the difference in lattice energies, and a transformation $1 \longrightarrow 2$ results. Fig. 4 illustrates [1b] the thermodynamic functions for the two crystal forms of tin. The curves of ΔH and $T\Delta S$ intersect at the transition temperature where $\Delta G = 0$.

Grey tin has four nearest neighbours at 2·80 Å and a cubic structure. White tin has four nearest neighbours at 3·016 Å and two at 3·175 Å and a tetragonal structure. At the transformation temperature of ~292° K direct calorimetry shows that the heat of transformation is about 522 cal.(g.-atom)$^{-1}$, and is compensated by the entropy difference. So far as is known, this transformation is discontinuous, although anomalous structural changes in tin [11] may imply some " forewarning ". This can

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[10] See Bridgman, " The Physics of High Pressures ", Bell, London, 1949.

[11] Arlman and Kronig, *Physica*, 1943, **10**, 795 ; Prasad and Wooster, *Acta Cryst.*, 1956, **9**, 35.

be given a structural interpretation to match the thermodynamic description. From the crystallographic standpoint, in a discontinuous transformation between independent phases a single crystal of one form changes into a random assemblage of (smaller) crystallites of the other form. If a single crystal is studied by one of the standard X-ray techniques, such as the obtaining of Laue photographs, then when it is taken round a cycle of temperatures including the transformation temperature, there should be no *persistence of crystal axes.*[12]

Specific tests for persistence of axes have not in fact yet been made for many interesting transformations which are apparently discontinuous thermodynamically. It can be predicted with some confidence that randomisation of the crystallites of the new structure, formed from the parent single crystal, must be quite marked for a discontinuous transformation to appear. Nevertheless absolutely complete randomisation of axes must be rare. The number of nuclei of the new form which grow into crystallites at the expense of a parent single crystal must be limited for kinetic and energetic reasons. Depending on the mechanism of crystal growth, the probability of formation of such nuclei may often show some preferred orientation with respect to the parent crystal lattice. From the structural point of view, randomisation of new crystallites is only complete in a polycrystalline assembly where averaging over many parent crystals can be made. A further consideration is that when a polycrystalline assembly is taken repeatedly through a thermal cycle traversing a transition, the new crystallites will ultimately become so small that their atoms become sufficiently mobile to exhibit grain growth. A " natural " lower limit for crystallite size in polycrystalline

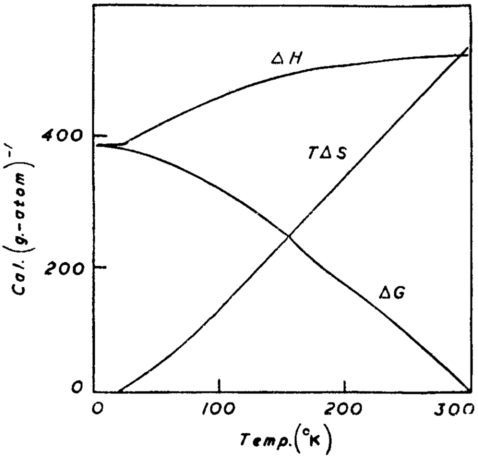

FIG. 4

Curves for the reaction grey tin ⟶ white tin.

[Reproduced from Lumsden, " Thermodynamics of Alloys ", Monograph, Institute of Metals, London, 1952, p. 94.]

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[12] Kennedy, Ubbelohde, and Woodward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 303.

transformations can be foreseen on these grounds. So far the only evidence for a natural limit arises for metals.

By way of an example of randomisation in a transformation, Plate 1 illustrates X-ray rotation photographs of crystallites of the stable polymorph α resorcinol which gradually appeared when a single crystal of β resorcinol was studied during many months at room temperature. If the α crystallites were completely randomised they would give perfect powder rings. Actually marked preferred orientations are observed, though so far as is known the reversible transition α to β is thermodynamically discontinuous.[13]

Up to the present, structural studies on discontinuous transformations have seldom been correlated with thermodynamic considerations. A suggestive general discussion has been given by Buerger.[7a] Some of the few examples for which there is both structural and thermodynamic information will now be considered.

(i) The transformation at 469° of cæsium chloride from body-centred cubic to face-centred cubic has been studied [14] by means of measurements on thermal expansion, intensities of X-ray reflections as a function of temperature, electrical conductance, and differences of heat content.

(ii) The transformations of rhombic into monoclinic sulphur at 95·6°, of α into β *o*-nitroaniline, and of yellow into red mercurous iodide have been studied by measurement of rates of evaporation and rates of movement of boundaries between phases, as well as by measurement of thermodynamic parameters.[15]

(iii) X-Ray powder studies of the transformation of rubidium and potassium halides from face- to body-centred cubic under pressure have been made.[16] Transformations occur at around 5000 atm. for the rubidium salts, and subdivision of grains is observed in the transformation indicating that it is structurally discontinuous.

(iv) X-Ray studies have been made on transitions of silver iodide under pressure.[17] A general discussion of transitions in silver halides has been given by Huggins.[7a]

(v) A variety of techniques has been applied for transitions in refractory metals.[18]

Continuous Transformations.—By contrast with the limited studies that combine structural with thermodynamic information for discontinuous transformations, a very large body of work has been carried out on transformations in solids which are, or appear to be, continuous.

Thermodynamic methods of study. In order to obtain some perspective, it is convenient to group methods of study. Many purely thermodynamic methods involve measurements of heat content, specific heat, or specific volume at different temperatures. Much less abundant information has

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[13] Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167**, 136.

[14] (*a*) Menary, Ubbelohde, and Woodward, *ibid.*, 1951, *A*, **208**, 158 ; (*b*) Harper and Ubbelohde, *ibid.*, 1955, *A*, **232**, 310.

[15] Hartshorne, *Discuss. Faraday Soc.*, 1949, **5**, 149.

[16] Jacobs, *Phys. Rev.*, 1938, **54**, 468.

[17] *Idem*, *ibid.*, p. 325.

[18] Jaeger, *Proc. k. ned. Akad. Wetenschap.*, 1940, **43**, 762.

been obtained on compressibilities, on shifts of transformation temperature under pressure, or on shifts of transformation temperature due to impurities. Polycrystalline samples have been used of somewhat indeterminate microstructure in practically all experiments, though the most recent work shows that the microstructure should be carefully specified in smeared transitions. In certain experiments the influences of crystal size and crystal perfection have been studied on phenomena such as hysteresis.[19] Attempts have also been made [20] to influence nucleation by ultrasonic vibrations in the transformation of solid hydrogen bromide, without perceptible effect (cf. Fig. 5).

Studies of specific volumes have the important practical advantage that prolonged observations can be made. This can be particularly significant in view of observations that near a transformation, rates of change in solids are frequently very slow.[21] Volume changes suffer, however, from the disadvantage that in many interesting transformations they are small, and are in any case difficult to correlate with other thermodynamic or structural changes. Techniques of study include dilatometric measurements on thermal transformations, based on linear coefficients of thermal expansion, determined either by optical comparators or by mechanical or optical interference methods, and have been applied to transformations in tungsten, iron, and nickel metals and in ammonium chloride.[4] Very numerous experiments have been made by using polycrystalline samples and a confining fluid, and transformations in sulphur and in ammonium and tetradeuteroammonium halides, sodium nitrate, copper sulphate pentahydrate, am-

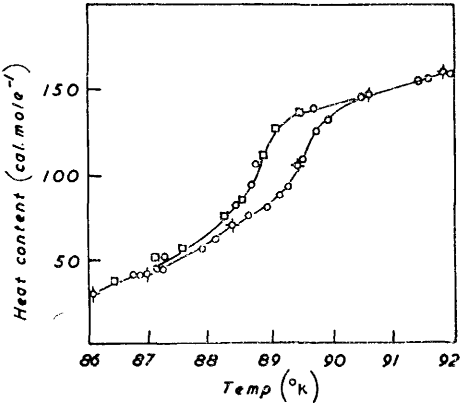

FIG. 5

Change of heat content of solid hydrogen bromide around T_c.

The curves are conventional hysteresis curves, and the points were determined in experiments with ultrasonic vibrations.

[Modified from Eucken, *Z. Elektrochem.*, 1939, **45**, 126.]

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[19] Thomas and Staveley, *J.*, 1951, 1420, 2572 ; Thomas, Staveley, and Cullis, *J.*, 1952, 1727.

[20] Eucken, *Z. Elektrochem.*, 1939, **45**, 126.

[21] Temperley, " Changes of State ", Cleaver-Hume Press, 1956, pp. 33, 41.

monium dihydrogen phosphate, and ammonium dichromate; also in resorcinol [12] and ammonium chloride.[22] Suitable confining fluids are, however, difficult to find, especially for use at temperatures above about 250° c. *X*-Ray methods have been increasingly used to evaluate the thermodynamic parameters at both high and low temperatures for polycrystalline samples and for single crystals; applications include transformations in nickel, sodium nitrate, ammonium chloride, bromide, and iodide,[4] and in $M_2H_3IO_6$ where $M = Ag$ or NH_4.[23]

Calorimetric studies, if they involve the conventional electrical heat-input calorimeter, may give artificially smoothed specific-heat curves because of the slowness of certain changes in crystals and the difficulty of testing for equilibrium, especially near the peak temperature T_c of a thermal transformation. This fact makes mathematical arguments about the precise shape of a specific-heat curve near T_c difficult to test in reality. Nevertheless, plots of the excess of specific heat ΔC_p in an anomaly over the normal value for crystal vibrations give basic thermodynamic information about the transformation, since they permit estimates of the total entropy change involved. Usually the integral need only be taken over a quite narrow range of temperature:

$$\Delta S_{\text{transf.}} = \int_{T_1}^{T_2} \Delta C_p \,\mathrm{d} \ln T$$

Calorimetric studies of transformations have been made for many solids in the course of evaluation of standard entropies by means of the Nernst heat theorem. Many examples up to 1948 have been collected in ref. 4; transformations studied in other ways mentioned in this Review have generally also been studied by calorimetry; individual references are not given where no new points of major significance arise.

In certain instances attempts have been made to analyse the specific-heat curves in detail. For example, entropy changes for the ellipsoidal and tetrahedral molecules quoted below have been carefully evaluated in a number of cases.[24] These support the view that the transformations involve at most hindered rotation above T_c with potential barriers separating minima of potential energy. There is little real evidence for free rotation in most crystals. Computations of the increase in entropy in some of the transformations leave no doubt that some form of randomisation of structure is taking place on passing from low to high temperatures. For example, in ammonium chloride above T_c, $C_V \sim 9\boldsymbol{R}$. Subtracting the contribution to the specific heat due [24] to lattice vibrations, $C_{\text{vib.}} = 6\boldsymbol{R}$, this leaves $(C_V)_{\text{orient.}} = 3\boldsymbol{R}$ above T_c. If there were free rotation, $C_V \approx 3\boldsymbol{R}/2$; librations about equilibrium orientations in the crystal are indicated by this evidence.

For hydrogen and deuterium chloride, bromide, and iodide determination of the entropies of transformation [24] gives a value of *n* in the Boltzmann

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[22] Mitsui and Furuchui, *Phys. Rev.*, 1953, **90,** 193; 1954, **95,** 558.

[23] Baertschli, *Helv. Phys. Acta*, 1945, **18,** 267.

[24] Zimm, Oriani, and Hoffman, *Ann. Rev. Phys. Chem.*, 1953, **4,** 219.

expression $\Delta S_{\text{transf.}} = \boldsymbol{R} \ln n$ for these halides of $n \sim 4{\cdot}5$, except for hydrogen bromide where it is near 3·2. Here n refers to the number of alternative orientations above T_c. In a body-centred cubic lattice, as assumed by the hydrogen halides above T_c, the molecules may occupy six alternative positions so that the maximum value for $\Delta S_{\text{transf.}} = \boldsymbol{R} \ln 6$. Reasons why the computed value lies somewhat below the maximum have not been found.

Structural origins of entropy increases in transformations in solids

The principal types of randomisation that have been suggested to account for the anomalous entropy increases in crystals include the structural changes now discussed.

Positional Randomisation in Solids.—In certain crystals consisting of spherical or almost spherical units in close packing, the continuous transformations observed can be attributed to randomisation of position of certain units of structure with regard to the ideal crystal lattice. One example in ionic crystals is the transformation of β into α silver iodide. Above 146° X-ray and conductance evidence indicates that the Ag^+ cations have their positions randomised.[25] In addition to occupying sites in the ideal lattice, the Ag^+ cations occupy alternative sites at random. Various other silver salts which exhibit transitions have been reviewed.[17, 26] Conductance and X-ray evidence suggests [27] that analogous randomisation of Na^+ and F^- occurs in cryolite above about 880°.[27] In metals randomisation of position is observed with a critical temperature, T_c, in various order–disorder transformations in alloys. Below T_c the atoms of the alloy occupy specific positions on a superlattice; random positions with respect to the same lattice points are assumed above T_c.[28]

Orientational Randomisation in Solids.—In many crystals, polyatomic units of structure can become randomised in orientation with respect to neighbouring groups above a critical temperature T_c which depends on the crystal forces. It was originally suggested [29] that above T_c these polyatomic groups were rotating freely, thereby acquiring effective rotational point symmetry about one or more axes. Thermodynamic evidence quoted above and various structural studies have shown that alternative orientations with different minimum potential energies U_1, U_2, U_3 . . . are present in many crystals. As the temperature rises, the orientation of the asymmetric units becomes randomised with respect to these alternative positions (cf. Fröhlich, ref. 7*b*).

Polyatomic groups of ellipsoidal symmetry. Many solids in which the units of structure have approximately ellipsoidal shape show transformations involving randomisation of orientation. Transformation temperatures are generally higher the higher the lattice forces, but even for the halogen acids

[25] Krieger and James, *J. Chem. Phys.*, 1954, **22**, 796.

[26] Pitzer, *J. Amer. Chem. Soc.*, 1941, **63**, 512.

[27] Landon and Ubbelohde, *Proc. Roy. Soc.*, 1957, *A*, **240**, 160.

[28] Elcock, " Order–Disorder Phenomena ", Methuen, London, 1956; see also other discussions in refs. 4 and 7.

[29] Pauling, *Phys. Rev.*, 1930, **36**, 430.

quite complicated relations are found.[24, 26] Many other diatomic molecules whose crystals exhibit " randomisation of orientation ", are quoted in ref. 3.

Randomisation of orientation of tetrahedral molecules. A great variety of non-thermodynamic methods of study have been applied in the attempt to elucidate what is happening to anomalous thermal transformations in solids.

Tetrahedral molecules exhibit transformation temperatures T_c which rise as the crystal potential barriers opposing randomisation of orientation increase. Thus for molecules interacting with van der Waals forces in the crystals, though there is some uncertainty about the nature of the transition for the larger molecules,[7a] the sequence of T_c found is methane, 20° K ; silane, 63° K ; carbon tetrafluoride, 77° K ; *neo*pentane, 140° K. For comparable transformations in ionic lattices, for ammonium salts containing tetrahedral groups there is a jump to higher temperatures around 240° K.

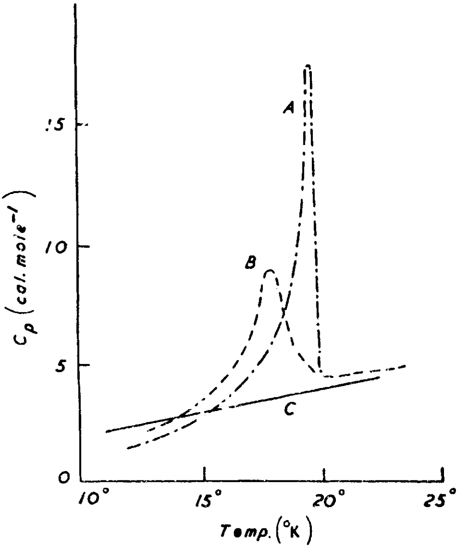

FIG. 6

Effect on the lambda-point anomaly of dilution of solid methane by krypton.
A, 3·70% Kr ; *B*, 7·45% Kr ; *C*, 50·22% Kr and above.

[Reproduced from Ubbelohde, " Modern Thermodynamical Principles ", Oxford Univ. Press, 1952, p. 83.]

One significant way of experimenting with potential barriers opposing randomisation of orientation in crystals is to dilute the crystal lattice with more symmetrical molecules or atoms so as to reduce the barrier. For example, Fig. 6 illustrates the effect on the specific heat anomaly of bringing progressively more krypton into solid solution in methane.[30] The steepness of the co-operative change rapidly decreases with increasing dilution of

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[30] Eucken and Veith, *Z. phys. Chem.*, 1938, **38**, *B*, 393.

the non-spherical methane molecules. A corresponding effect has been studied for the " rotation " of benzene in its crystals, below their melting point.[31]

An interesting shift of transformation temperature occurs on substituting isotopes ; effects can be particularly striking when deuterium is substituted for hydrogen in the crystals. When hydrogen bonds are present, the substitution of deuterium for hydrogen alters zero-point energies and affects the overlap of alternative structures in the crystals. The shift of transformation temperature is often quite large ; it is difficult to predict quantitively, but the general qualitative influences can be understood.[32] When hydrogen bonds are absent, the principal effect of substituting deuterium for hydrogen is to raise the moments of inertia of rotators and the reduced masses of vibrators in the crystals by amounts which can be readily calculated. The repulsion envelopes of the deuterium-substituted molecules also undergo a small shrinkage owing to a decrease [33] in the zero-point energies of the valency bonds. In the absence of other complicating factors this shrinkage should lead to effects on the transformation parameters comparable with those of increasing the external pressure on the hydrogen compounds, but no complete tests of such effects can yet be made. In the case of crystalline methane, it is interesting to note that substitution of deuterium for hydrogen leads to a doubling of the lambda peaks with a general shift of the upper peak to higher temperatures : thus methane has one value of T_c at 20·4° K and monodeuteromethane and tetradeuteromethane have double peaks at 15·5°, 22·6° K and 21·4°, 26·3° K respectively. Increasing the pressure on crystalline methane also leads to a doubling of the lambda peaks, in conformity with the general statements made above.[34] The appearance of more than one lambda peak is strong evidence that the transformation involves orientational randomisation but not free rotation in the crystals.

In solid solutions of methane in tetradeuteromethane the upper peak varies in a regular way as the mole fraction of CH_4 increases, but the lower peak is pushed downwards and is eventually suppressed.[4]

Other types of randomisation of orientation. Corresponding randomisation can occur in favourable cases for molecules whose approximation to figures of rotation about one or more axes is even less close. Only selected examples can be quoted here. In benzene, rotation in the crystals about the hexad axis seems borne out by various lines of evidence discussed below.[35] In some polymethylenic paraffins, orientational randomisation about the long-chain axis seems likely in the crystals below the melting points.[36] Organic compounds of higher molecular weight, such as hexamethylbenzene, also

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[31] Thompson and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46,** 349.

[32] Ubbelohde and Gallagher, *Acta Cryst.*, 1955, **8,** 71.

[33] Ubbelohde, *Trans. Faraday Soc.*, 1936, **32,** 526.

[34] For the rise in T_c when deuterium is substituted for hydrogen, and the doubling of the peaks for methane under pressure, see Kruis, *Z. phys. Chem.*, 1940, **48,** *B*, 321.

[35] Andrew and Eades, *Proc. Phys. Soc.*, 1953, **218,** *A*, 537 ; Frühling, *Ann. Physique*, 1951, **6,** 401.

[36] Ubbelohde, *Trans. Faraday Soc.*, 1938, **34,** 289.

exhibit orientational randomisation.[37] Transformations in crystals of organic molecules with tetrahedral symmetry, with the general formula MX_4, have been studied by Backer and Perdok.[38]

In tetramethylthiomethane $C(SCH_3)_4$, for example, *X*-ray and thermodynamic studies show transformations as follows :

$$\underset{\text{Tetragonal}}{\text{I}} \xrightarrow{23{\cdot}2^\circ} \underset{\text{Tetragonal}}{\text{II}} \xrightarrow{45{\cdot}5^\circ} \underset{\text{Cubic}}{\text{III}} \xrightarrow{65{\cdot}5^\circ} \text{Melt}$$

Even in the cubic phase, the molecules are found not to be rotating freely, since insufficient space is available in the crystal lattice. Randomisation of orientations in different directions does however take place at the 45·5° C transformation. For these crystals, specific-heat measurements and dielectric studies confirm the absence of free rotation of even the methylthio-groups in the melt. Amongst inorganic compounds, a group of nitrates of the general formula MNO_3 has been studied in some detail ; [39] for these and other inorganic examples see ref. 2.

Transformations at Constant Volume.—Both classes of entropy increase discussed earlier pass through a more or less pronounced maximum rate of increase, where the additional specific heat passes through a peak value. This kind of behaviour is characteristic for energy increases in solids in which the magnitude of the energy jumps for individual units of structure depends on the number of units already in the higher-energy state. Normally the energy jump decreases as more units of structure assume the higher-energy state, and the autocatalytic process of energy uptake accounts for the lambda shape of the curve for the excess of specific heat due to the co-operative change in question.[40] When the transformation takes place with increase in volume, as often happens, the progressive expansion of the crystal lattice resulting from progressive energy jumps lessens the energy barriers and in part explains the autocatalytic nature of the transformation. This explanation is confirmed by calculating the specific-heat anomaly for a change carried out at constant volume instead of at constant pressure. Fig. 1 shows that the sharp lambda character is almost entirely suppressed at constant volume.[41] Measurements of the compressibilities are required to convert values of C_p into values of C_v. Quite large shifts of transformation temperature are involved ; *e.g.*, for ammonium chloride the lambda transition at $-31°$ shifts to $+30°$ at 9500 atm.

Structural Aspects of Other Co-operative Transformations in Solids.—Many transformations in solids are known whose structural origin is more complex than the two types described above, but in which the autocatalytic decrease of the restraining crystal fields follows the same general pattern

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[37] Huffman, Parks, and Daniels, *J. Amer. Chem. Soc.*, 1934, **56**, 1513 ; Andrew, *J. Chem. Phys.*, 1950, **18**, 607 ; Saki and Chihara, *Sci. Papers, Osaka Univ.*, 1949, Nos. 1 and 2.

[38] Backer and Perdok, *Rec. Trav. chim.*, 1943, **62**, 533.

[39] Finbak and Hassel, *Z. phys. Chem.*, 1937, **35**, *B*, 25 ; 1937, **37**, *B*, 468.

[40] For an elementary discussion see Ubbelohde, " Modern Thermodynamical Principles ", Oxford Univ. Press, 1952, 2nd edn.

[41] Lawson, *Phys. Rev.*, 1940, **57**, 417.

with changes of temperature or volume. Some of these structural effects can be briefly summarised as follows.

(i) *Transformation from a paraelectric to a ferroelectric solid.* In this transformation at high temperatures, individual molecular dipoles in the crystal behave more or less independently in the paraelectric state. Below T_c the dipole fields co-operate to give a much higher total polarisation in the so-called ferroelectric field.

Transformations of this kind are known for a range of acid phosphates and arsenates of the general formula MH_2XO_4 where M is an alkali-metal atom, and X = P or As. Effects of isotope substitution on the transformation temperature are interesting and may be illustrated by the figures in Table 1. A group of titanates of the general formula $M^{2+}[TiO_3]^{2-}$ show similar effects, which in some cases are of considerable technical importance.[2] Related crystals such as $NaNbO_3$ behave in a similar way.[42] Examples from other types of structure seem likely to arise, but have not been studied extensively.

TABLE 1

Salt	T_c(H)	T_c(D)
$KNaC_4H_4O_6,4H_2O$*	255—258°	250—251°
KH_2PO_4	122	213
$(NH_4)H_2AsO_4$	215·8	298·6
KH_2AsO_4	95·6	162·0
RbH_2AsO_4	109·9	177·8
CsH_2AsO_4	143·3	212·4

* Rochelle salt.

(ii) *Transformations from paramagnetic (high-temperature) to ferromagnetic (low-temperature) crystals.* These involve co-operative reinforcements of the magnetic dipoles below T_c. Such changes have long been known for certain metals of transitional elements, including iron ($T_c = 780°$) and nickel ($T_c = 365°$ c). In recent years related transitions have been discovered in a number of crystal compounds such as the ferrites of general formula Fe_2MO_4, where M is a bivalent metal such as copper, magnesium, lead, or nickel.

(iii) *Transformation from paramagnetic (high-temperature) to antiferromagnetic (low-temperature) crystals.* These involve complete or partial co-operative neutralisation of magnetic dipoles below T_c by coupling of magnetic spins in opposition. Examples include $NiCl_2$, MnO, FeO, NiO, and probably Cr_2O_3. Each of these crystals exhibits a transformation with specific-heat anomaly accompanying the magnetic change.[43]

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[42] Vousden, *Acta Cryst.*, 1956, **7**, 321.

[43] Street, *Research*, 1951, **39**, 258; Shull and Smart, *Phys. Rev.*, 1949, **76**, 1256; Smart and Greenwald, *ibid.*, 1951, **82**, 113.

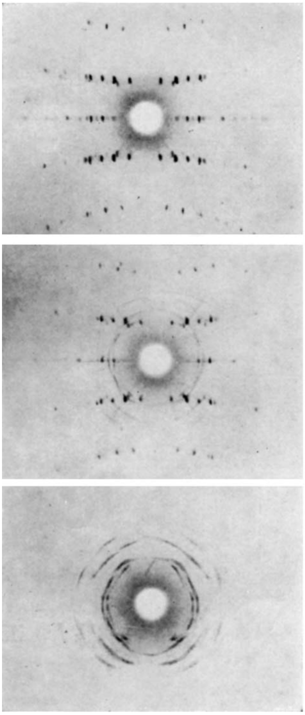
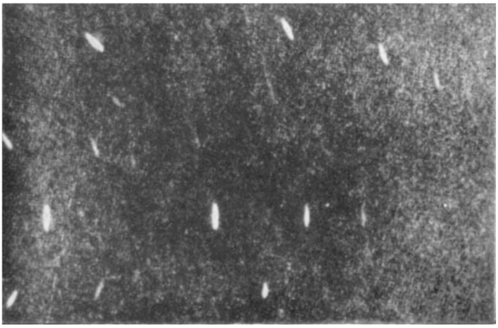


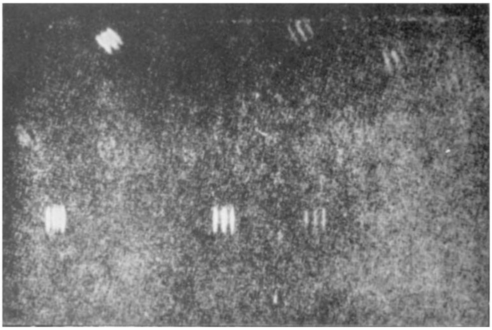
PLATE 1

X-Ray rotation photographs of spontaneous reversion of a single crystal of β resorcinol (top) to crystallites of α resorcinol (bottom) with preferred orientation. The central picture shows incipient formation of the α crystallites.

[Reproduced from Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167**, 136.]



(*a*)



(*b*)

Plate 2

Coexistence phenomena in potassium dihydrogen phosphate.

(*a*) Laue photographs of single crystals around 123° K.

(*b*) Same crystal showing split reflections below 123° K.

[Reproduced from Ubbelohde and Woodward, *Nature*, 1945, **156**, 21.]

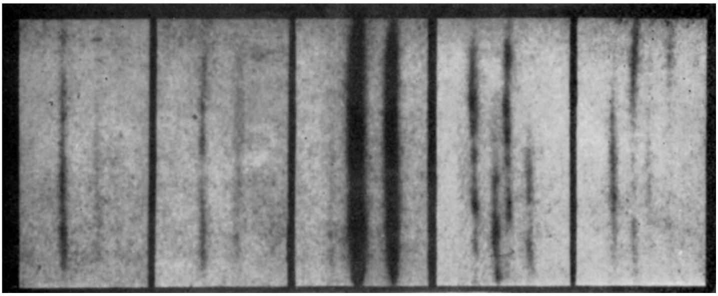


Plate 3

Coexistence phenomena in ammonium chloride. Bragg X-*ray photographs exhibit coexistence in the three right-hand pictures around* T_c, − 31°.

[Reproduced from Dinichert, *Helv. Phys. Acta*, 1944, **17**, 338.]

Structural techniques for studying changes accompanying transformations in solids

The above summary of structural changes occurring in various transformations in solids is based on conclusions from a great variety of non-thermodynamic methods of study which have been applied in the attempt to elucidate the nature of the changes taking place. These will now be briefly reviewed.

X-*Ray methods.* Whatever other methods are applied, the study of a thermal transformation can hardly be regarded as complete until X-ray techniques have been used. Earlier applications of X-ray methods involved practically exclusively the taking of powder diagrams. These give useful information, averaged over a large number of crystals ; modern precision powder methods are often of particular value when the temperature of transformation is remote from room temperature. For example, with particular reference to a principal theme in this Review, coexistence phenomena in powder diagrams have been claimed in a transformation in MnO,[2] and in order–disorder transformations in Pt–Co and in Cu_3–Au alloys (cf. ref. 28, pp. 137, 138). But powder diagrams do not make it clear how intimate the interpretation of two closely related structures can be. When single crystals are used, X-ray methods give additional information of the highest importance for interpreting transformations in solids. Additional observations of special significance include : (i) The detection of coexistence of regions of two alternative structures within a hybrid single crystal (the terminology follows that of ref. 9) around the transformation temperature T_c. This phenomenon has been observed by means of both Bragg and Laue photographs in single crystals of substances such as Rochelle salt and potassium dihydrogen phosphate [9] and ammonium chloride,[44] also in various titanates [45] and in other cases listed in ref. 2. There are reasons to infer the presence of this phenomenon in other transformations where its existence has not yet been specifically detected.

One way of describing the phenomenon of coexistence of sub-regions of two slightly different structures in a hybrid single crystal is to consider what happens when a true single crystal of one structure is examined, starting well below the peak transformation temperature T_c. Normal single-crystal Bragg or Laue photographs are obtained of the low-temperature structure. If the crystal is gradually warmed, rushed heating being avoided since strains develop, sub-regions of the second slightly different structure appear near T_c. In any one single crystal the precise temperature at which such sub-regions appear will often vary over a few degrees.[46] This is partly due to the probability of growth of the new structures depending on chance factors, and partly due to a real shift of the free energy of the sub-region according to its surface area within the hybrid single crystal, and according to its state of strain. The size of such sub-regions varies from crystal to crystal. One estimate for potassium dihydrogen phosphate indicates an

[44] Dinichert, *Helv. Phys. Acta,* 1944, **17,** 338.

[45] Blattner, Känzig, Merz, and Sutter, *ibid.,* 1948, **21,** 207.

[46] Gallagher, Ubbelohde, and Woodward, *Acta Cryst.,* 1955, **8,** 561.

upper limit for the sub-region edge of 5×10^{-3} cm. In Rochelle salt, sub-regions [9] may be about 10^4 Å across. These are however only tentative estimates.

It is important to use precision thermostats (such as those described in refs. 9, 12, 14*a*, and 47) around the transformation temperature T_c to follow what happens as it is traversed. As the temperature rises more and more regions of the high-temperature structure 2 appear, until the hybrid single crystal is completely transformed into structure 2, somewhat above T_c. If this crystal is cooled again, the changes are traversed in the reverse sense. It is not yet clear whether the identical sub-regions appear, though internal defects in the single crystal probably impose preferred growth patterns for the sub-regions. The temperatures at which a given proportion of the hybrid crystal consists of sub-regions of one form need not be the same in the direction $1 \rightarrow 2$ as in the direction $2 \rightarrow 1$, for reasons of hysteresis (p. 267).

(ii) Hybrid single crystals around a transformation region may be regarded as a structural alternative to the discontinuous transformation of structures already described.

The difference arises as follows : For geometrical reasons, nucleation of a new structure generally occurs with preferred orientation with respect to the matrix from which it is formed. This preferred orientation can become so close to a unique choice that the whole crystal transforms with effective " persistence of axes ".[12] When the difference in structure between the low-temperature and high-temperature arrangements is sufficiently small, the appearance of regions of 2 within a matrix of 1 does not involve sufficient mechanical strains to lead to break-away of the new crystallites. If the orientation of regions of the new form is sufficiently close to the orientation of the matrix, and if there is no break-away of crystallites, the hybrid crystal survives as a unit, though it passes through a state of maximum strain energy around T_c where regions of the two structures coexist in comparable amounts.

Coexistence can be illustrated in various ways. For example, Bragg and Laue photographs show " splits " in the hybrid region, which are illustrated on Plates 2 and 3.

This brief description should make it clear that in addition to giving information about coexistence of two structures within a hybrid (*a*) single-crystal *X*-ray photographs can establish how nearly the two structures actually correspond around T_c. This can in principle also be done by precision powder photographs but single-crystal exposures are much more satisfactory. By way of example, in potassium dihydrogen phosphate there is coexistence between oppositely polarised sub-regions (+ 1 and − 1) of monoclinic structure, which depart from tetragonal structure by only 27′ of arc.[9] Around T_c these coexist with tetragonal sub-regions.[2] In Rochelle salt [9] the monoclinic sub-regions of + 1 and − 1 depart from orthorhombic by only 12′ of arc. Around T_c they coexist with sub-regions of orthorhombic.[2] In ammonium chloride there is coexistence between

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[47] McKeown, *J. Sci. Instr.*, 1954, **31**, 271.

regions of cubic symmetry of lattice spacing 3·8540 Å and 3·8480 Å (see p. 268).

(*b*) Single-crystal X-ray photographs can determine how far crystal axes actually persist in a " single crystal " in a cycle of temperature changes traversing T_c. This kind of investigation has at present been made only for some single-crystal nitrates [12] and cyanides.[48] It throws into sharp relief the antithesis between thermodynamic methods of describing phase transformations, which refer to statistical averages, and structural methods in which the behaviour of individual co-operative assemblies such as a hybrid single crystal are under examination.

For transformations in substances other than those quoted, it may be expected that many intermediate degrees of persistence of axes will be found. Transformations in which the persistence of axes of new crystallites is so nearly perfect that they appear as continuous (though possibly with hysteresis) present one extreme. Transformations in which any persistence is negligible, so that an absolutely sharp discontinuous phase transformation may be expected, form the other extreme.

(*c*) X-Ray photographs can give important additional information in favourable cases about the state of strain and the internal surface of a single crystal. Though such applications of X-rays are well known for metals [49] they have not been at all extensively developed for transformations in solids.[12] After a substance has traversed a continuous transformation which involves coexistence of sub-regions, the state of strain may persist above T_c for a period of time ; in the case of barium titanate it is several hours.[50]

Near a thermodynamic transformation in a crystal, X-ray methods frequently show abnormal changes in the intensities of certain reflections. This has been observed for both continuous and discontinuous transformations, for example in cæsium chloride,[14a] sodium cyanide,[51] and quartz.[52] One source of such changes can arise from changes of extinction. If there is a premonitory increase of co-operative lattice defects, or even if there is the appearance of sub-regions of the alternative structure, as T_c is approached, extinction would be expected to decrease. Lattice disorder would however lower the intensity of reflection in any one direction. A more subtle effect could arise if one crystal structure became thermodynamically unstable with respect to a related structure as the temperature rises, because the high-temperature structure provides a framework permitting considerably greater amplitudes of vibration with consequent enhanced vibrational entropy compared with the low-temperature structure. Such a possibility would almost certainly influence the intensities of selected X-ray reflections near T_c, but no clear instances have yet been established.

[48] Cimino, Parry, and Ubbelohde, unpublished work ; Bijvoet and Verweel, *Rec. Trav. chim.*, 1935, **54,** 631.

[49] Taylor, " Introduction to X-Ray Metallography ", Chapman and Hall, London, 1945.

[50] Känzig and Maikoff, *Helv. Phys. Acta*, 1951, **24,** 343.

[51] Siegel, *J. Chem. Phys.*, 1949, **17,** 1146.

[52] Gibbs, *Proc. Roy. Soc.*, 1925, *A*, **107,** 561.

Amplitudes of vibration in certain directions in a crystal which increase abnormally as the temperature rises may be accompanied by abnormal thermal expansion when the crystal structure permits it. The abnormal expansion as the transformation of certain nitrates is approached provides one example (see ref. 4).

Other Structural Techniques.—Other methods of investigation of structure have been applied in very considerable diversity to explore certain transformations in solids. Illustrative examples are discussed below, though these do not aim to be exhaustive (see refs. 4, 7). As an alternative to X-rays, neutron diffraction has been applied. This can be particularly useful in the special case where the atoms are carriers of permanent magnetic moments. For example, in the transformation paramagnetic to antiferromagnetic crystal, neutron diffraction shows how the spins are paired in layers in the crystals in the low-temperature form.[45] Neutron diffraction is also particularly valuable for studying transformations in crystals containing hydrogen bonds, as in potassium dihydrogen phosphate.[53] Direct location of the hydrogen or deuterium atoms can be made in favourable cases. Neutron diffraction confirms that above T_c the orientation of protons in ammonium chloride and of deuterons in ND_4Cl is randomised without free rotation.[54] Electron diffraction does not seem to have been used in any important instances.

Skilful use of the microscope can give useful supporting information about structural changes in transformations in solids, though the conclusions are necessarily more superficial. Studies of boundary movement [15] have already been referred to. Changes of grain size [55] in a conglomerate assembly of crystals, a hot stage and crossed Nicol prisms being used, indicate marked differences in the extent of break-up in different solid transformations. Extensive changes are claimed in potassium nitrate, ammonium nitrate, and silver iodide and only small changes in silver nitrate, thallium nitrate, sulphur, and resorcinol. The phenomena in a conglomerate are however dependent on a complex sequence of micromechanisms, and observations on single crystals are much to be preferred.

Conductance and dielectric studies on solids of high resistance. Various methods of measurement which introduce the time variable have given very valuable information in certain cases, though the results are not always easy to interpret uniquely. The most extensively developed involve the application of electric fields, with direct current to measure D.C. conductance, or alternating current using a wide range of frequencies to measure conductance and dielectric behaviour in cyclic fields. For example, in ionic crystals, D.C. conductance can be of special interest in revealing enhanced lattice defects in the neighbourhood of a transformation in solids; thus enhanced conductance is found around T_c in the transformations in nitrates.[12] This enhanced conductance falls away again above the region of pronounced coexistence of sub-regions of two related structures around T_c as the co-

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[53] Bacon and Pease, *Proc. Roy. Soc.*, 1953, *A*, **220**, 397.

[54] Zimm, Driani, and Hoffmann, *Ann. Rev. Phys. Chem.*, 1953, **4**, 207.

[55] Tammann and Boehme, *Z. anorg. Chem.*, 1935, **223**, 365.

operative defects introduced by coexistence " heal ". When the conductance is predominantly electronic, as in the transformation in cæsium chloride,[14b] plots of conductance against temperature point to premonitory effects in the crystals, before T_c is reached, and to hysteresis extending over about 15° in the transformation itself. Other examples studied in this way include mercuric iodide and silver iodide.[56]

Cyclic electric fields are particularly important in the case of solids containing polar molecules, since they give information both about dielectric constants and about the dielectric relaxation which becomes pronounced at critical frequencies in the solids. For example, dielectric constants measured not too near a critical frequency show pronounced increase of freedom of orientation above T_c of polar diatomic molecules such as the hydrogen halides.[4]

In principle, a study of the critical relaxation frequencies as a function of temperature for such solids should give important information about the crystal potential barriers opposing randomisation of orientation. However, these can be quite complex and will not in general be isotropic. Measurements on single crystals seem desirable in certain cases before the somewhat complex observations on relaxations can be interpreted.[57] At the comparatively high frequencies of visible light changes of refractive index, and changes from an isotropic to an anisotropic crystal structure in a transformation, have been used in favourable cases to give supporting information about transformations in solids. In certain cases the methods are quite sensitive. For example, before the *X*-ray studies of Ubbelohde and Woodward[9] definite evidence of a change in crystal structure in the transformation in Rochelle salt largely depended on optical measurements. For other applications of classical crystallographic methods see ref. 4.

Infrared studies can give useful information about transformations in favourable cases. For example, the absence of rotational fine structure above T_c in ammonium chloride lends support to the interpretation of a random distribution of molecular axes between two equilibrium orientations, rather than free rotation. Raman spectra for this salt are in general agreement with this view.[4]

Paraelectric–ferroelectric transformations. In this group of transformations of crystals containing polar molecules, the low-temperature form in a transformation shows a comparatively enormous enhancement of the dielectric constant. Various electrical studies which will not be detailed here (see ref. 2) show that the crystals pass from ordinary " paraelectric " behaviour to a behaviour which has been termed " ferroelectric " because of analogies with " ferromagnetism ". Ferroelectric crystals contain regions of co-operative dipoles, which can be identified with the sub-regions + 1 and − 1 in a hybrid crystal. A strong electric field brings all these regions to the same orientation because the co-operative action of the dipoles introduces only small changes of crystal structure. Many examples of

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[56] Jaffray, *Compt. rend.*, 1950, **230**, 525.

[57] Powles, *J. Phys. Radium*, 1952, **13**, 121.

coexistence of two related structures arise from transformations in solids of the type

ferroelectric	$\rightleftharpoons$	paraelectric
Structure with oppositely polarised domains + 1 and − 1		Structure 2

Magnetic measurements on transformations in solids. Many paramagnetic substances show co-operative interaction of magnetic dipoles below T_c. Such transformations exhibit many special features because of the long range of magnetic forces in co-operative systems, and will not be discussed in detail here. Typical paramagnetic–ferromagnetic transformations and paramagnetic–antiferromagnetic transformations have already been referred to.

Application of cyclic magnetic fields permits the study of relaxation times, and can give important information about the coupling between electron spins or nuclear spins in solids.[58] Paramagnetic relaxation studies have not as yet thrown much additional light on transformations in solids. Studies of nuclear magnetic resonance have proved to be of considerable importance when the interaction between neighbouring atomic nuclei of deuterium and hydrogen acting as spin carriers depends on whether the molecules containing these atoms are free to rotate in the solid, or are constrained in specific orientations. As the solids traverse T_c, studies of nuclear magnetic resonance [59] confirm marked increase of randomisation.

The transformation from conducting to superconducting solids involves some kind of co-operative interaction between the conduction electrons. Thermodynamic studies of the influence of diverse variables on the transition temperature [21] show some important analogies with other transformations in solids, but the subject as a whole falls outside the scope of this Review.

Miscellaneous techniques. For alloys undergoing order–disorder transformations,[28, 60] and for other electronic conductors,[14b] changes of electrical resistance throw important light on the change of order, since the conduction electrons are scattered by disorder in the crystal lattice. No complete correlation has been made between the scattering of conduction electrons and the scattering of, for example, X-rays, as the degree of order changes, though certain analogies can be found.[61] Other electronic properties such as the thermoelectric power or the thermal conductance should also exhibit anomalies around T_c, but have been left comparatively uninvestigated (cf. also ref. 28).

In principle any other property of a solid could be observed on traversing a transformation and could throw light on what is taking place. For

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[58] Cf. " Das Relaxationsverhalten der Materie ", ed. Müller, Steinkopff, Darmstadt, 1953.

[59] Richards, *Quart. Rev.*, 1956, **10,** 480.

[60] Nix and Shockley, *Rev. Mod. Phys.*, 1938, **10,** 1 ; Lipson, *Progr. Met. Phys.*, 1950, **2,** 1.

[61] Oldham and Ubbelohde, *Proc. Roy. Soc.*, 1940, *A*, **176,** 50.

example, for alloys Young's modulus changes significantly on passing from an ordered to a disordered state. As is the case for many other properties, this change exhibits hysteresis in the transformation.[62]

If the mechanism of a transformation involves coexistence of two closely related structures in hybrid single crystals a large internal surface will develop around T_c. Some of the experimental evidence for this has been previously reviewed.[2] It seems possible that the reported influence of various absorbed gases on the transformation temperature of solids [63] may arise from the influence of gases absorbed at large internal surfaces, around T_c, on hysteresis. Direct solid solution, leading to a depression of a true equilibrium temperature, does not seem thermodynamically an adequate explanation. Further experimental work seems desirable to investigate the phenomena reported, in the light of this suggestion.

Release of radioactive gases trapped in a solid at the transformation temperature forms the basis of Hahn's emanation method of searching for transformations. This release is almost certainly associated with increased lattice defects in the coexistence region.

Hysteresis.—One significant consequence of the coexistence mechanism of a smeared transformation is that it leads to a ready interpretation of hysteresis. When a system shows thermodynamic hysteresis, this means that it exhibits true equilibrium in certain respects, but not in others. The test of thermodynamic equilibrium always is to consider what happens when the system undergoes small fluctuations with respect to diverse variables. Solids exhibiting hysteresis always show temperature equilibrium, so that the vibrational partition functions *for the structures present* are always minimised. They may even show equilibrium with respect to vapour pressures, *for the structures present,* as appears to be the case for example in the palladium–hydrogen system [5] and in transformations of solids carried out in the presence of solvents. However, the minimum of free energy is not unique *with regard to all possible transformations of these structures themselves.* At any stage of the transformation, the structure depends on previous history. It is easy to see, for example, that if the change 1 to 2 occurs with increase in volume, sub-regions of 2 formed in a matrix of 1 will be in compression, whereas sub-regions of 1 formed in a matrix of 2 are formed in tension. Starting well above or well below T_c, the transformation curve will never follow exactly the same path. This is best illustrated from observations on single crystals, as in the transformation (Fig. 7) of Rochelle salt [9] or the measurements of lattice spacing (Fig. 8) of ammonium chloride.[44]

Many more studies of hysteresis have been made on polycrystalline samples than on single crystals. These do not permit the same detailed interpretation from the standpoint of the phase rule, but the averaging which takes place with polycrystalline samples provides useful statistical smoothing. Staveley and his co-workers [19] have pointed out that in a group of related ammonium salts the width of the hysteresis loop increases as the

[62] Siegel, ref. 7*a*, p. 379.

[63] Forestier and Kiehl, *Compt. rend.*, 1950, **230,** 2288 ; Kiehl, *ibid.*, 1952, **234,** 943.

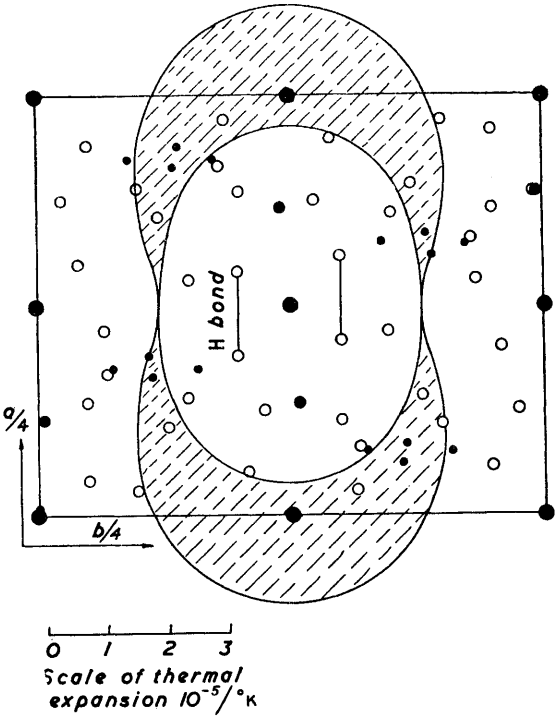

FIG. 7

Hysteresis limits in thermal expansion of Rochelle salt in the direction of the a axis around — 4° ; projection on (001).

[Reproduced from Ubbelohde and Woodward, *Proc. Roy. Soc.*, 1946, *A*, **185**, 448.]

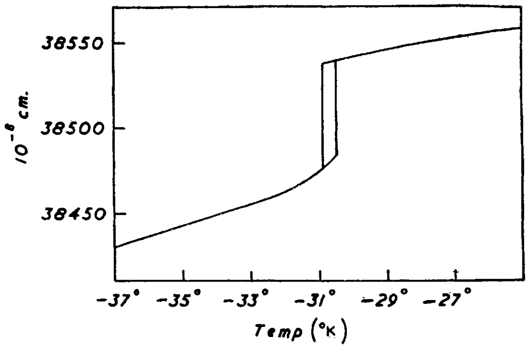

FIG. 8

Lattice spacing of ammonium chloride showing hysteresis around T_c.

[Reproduced from Dinichert, *Helv. Phys. Acta*, 1944, **17**, 338.]

volume change increases, as might be expected from the considerations outlined earlier (see Table 2).

In all these studies co-operative fluctuations of much greater magnitude than appears kinetically possible[64] would have to take place in order to dissipate hysteresis completely. Experimental tests on the hysteresis in the volume transformation in solid hydrogen bromide[20] are illustrated in Fig. 5. The various attempts to catalyse fluctuations by ultrasonics or other means failed to shift the hysteresis curve, thus verifying that this represents a path of metastable or neutral equilibrium. Reduction of the crystal size in ammonium chloride[19] or replacement of one isotope by another[13, 19] can have a marked effect on hysteresis, but precise theories about how these changes affect the barriers between coexistent regions of slightly different structures have not yet been put forward. Other properties may also throw a valuable light on hysteresis.[63]

TABLE 2

T_c(° C)	Salt	ΔV transf. (cm.^{3} mole^{-1})	Width of hysteresis loop (° C)
234·4	NH_4Br	0·03	0·06
247·95	NHD_3Cl	0·07	0·07
214·9	ND_4Br	0·08	0·11
244·6	NH_3DCl	0·11	0·12
242·6	NH_4Cl	0·15	0·35
223·4	$(NH_4)_2SO_4$	0·35	1·2
168·1	ND_4Br	0·6	9·0

These considerations suggest that attempts to make direct observations on shifts of the barriers between coexistent regions in hybrid single crystals should prove particularly valuable when the rather difficult experimental techniques can be mastered. Up to the present, such studies appear to have been limited chiefly to single crystals in ferroelectric–paraelectric transformations. For example, direct movements of + and − sub-regions in hybrid single crystals under the influence of a polarising field have been observed between crossed Nicol prisms[22] in the case of potassium dihydrogen phosphate. At the Curie point the transformation propagates with a velocity of about 2 cm. min.$^{-1}$. Many mathematical theories of hysteresis introduce theoretical difficulties which lie outside the scope of this Review, but a brief list of references may be given.[65]

Conclusions

The Structural–Thermodynamic Interpretation of Transformations in Solids.—From what has been said, certain structural aspects of transforma-

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[64] Ubbelohde, *Trans. Faraday Soc.*, 1937, **33,** 1203.

[65] Everett *et al.*, *ibid.*, 1952, **48,** 749 ; 1954, **50,** 187, 1077 ; 1955, **51,** 1551 ; Hartmann, *Z. phys. Chem.*, 1942, **52,** *B,* 338 ; Enderby, *Trans. Faraday Soc.*, 1955, **51,** 835 ; 1956, **52,** 106.

tions in solids indicate significant modifications which must be made to the mathematical theory.

In the first place, " phases " can only behave as really " independent " when they (*a*) differ substantially in specific volume and molecular arrangement, and (*b*) are generated in portions of phase space that do not require any other phase for their complete description. In this sense, a vapour phase is independent of the solid phase in equilibrium with it, except possibly at very high gas densities. On the other hand, when one solid structure is unavoidably generated in a matrix of another, as in hybrid single crystals, the two phases are not independent.

This remark suggests that if it were possible to effect a solid transformation which is usually continuous or smeared, by way of the vapour phase as intermediary, a discontinuous transformation would be observed. At first sight this seems likely. However, consideration of the theory of thermodynamic fluctuations suggests that whenever the difference between the structures and free energies of two arrangements is small, both will arise spontaneously in coexistence around T_c. In this sense coexistence is a necessary phenomenon, not an accident of the kinetic mechanism of structural transformations.

In the above discussion of some of the structural problems that arise in connection with thermodynamic transformations as actually observed in solids, the question has been left open whether any ideal experimental procedure might be devised in which transformations could take place without the introduction of any " arbitrary " terms in the neighbourhood of the peak transformation temperature. Another way of stating this question is to inquire whether the factors in the complete partition function for the solid around T_c can all be given unique equilibrium values, as is generally assumed in the theory of statistical thermodynamics. This ultimately depends on relaxation times for finite departures from these equilibrium values. Finite departures in sub-regions of a crystal can arise from the kinetic mechanisms followed in a transformation. Finite departures in sub-regions may also be required by the theory of thermodynamic fluctuation for an ideally continuous transformation irrespective of the kinetic mechanism followed. When relaxation times are large, as must be the case for certain types of co-operative fluctuations,[64] some degree of thermodynamic arbitrariness seems unavoidable in the transformation whether discontinuous or even ideally continuous, merely because the time scale of ordinary experiments happens to be much finer than the time scale for *structural* fluctuations.

When there is coexistence of two structures 1 and 2 modification to the phase rule becomes necessary. As already stated, extra terms for the strain energy ξ_{12} and the internal energy η_{12} must be added to the usual independent variables that determine the free energy. For two structures that show coexistence around T_c the free-energy equations can be written

$$G_1 = \mathrm{f}_1(p, T, \xi_{12}, \eta_{12})$$
$$G_2 = \mathrm{f}_2(p, T, \xi_{21}, \eta_{21})$$

The extent to which the additional variables can modify the standard free energy $G = f(p, T)$ is limited by physical factors. The strain energy ξ_{12} must not exceed the breaking strength of the hybrid crystal since otherwise an " independent " if strained new structure will result. The internal surface energy η_{12} of atoms or molecules situated at surfaces of separation between sub-regions of 1 and 2 must not exceed the activation energy for self-annealing, since otherwise one region will grow at the expense of its neighbours by migration of the atoms or molecules, and so lower G.

Within these limits, the operation of these additional " variables " leads to a modified phase rule for solids, as already stated.[5] Since these additional variables can change from place to place within a single crystal, they are not to be regarded as " independent ", but " arbitrary " within limits.

It is easy to see that when structures 1 and 2 coexist over a narrow range of temperature, instead of the G_1 and G_2 surfaces giving a clean intersection at a curve, as is required by the classical phase rule, they will give a " smeared intersection " which simulates the geometrical contact postulated on mathematical grounds for phase transitions " of higher order " (Fig. 9).[66] In cases where this structural interpretation of continuous transitions must be applied, purely mathematical theories of continuous transitions are misleading. There are reasons for believing that this interpretation of continuous phase transitions in terms of the coexistence of two closely similar structures within hybrid single crystals around T_c is in fact very general, though direct X-ray verification has so far proved possible in a few cases only.

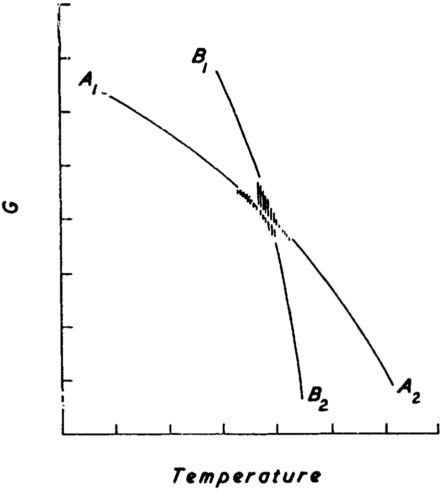

FIG. 9

Smeared transitions due to indeterminate intersection of two free-energy curves.

[Reproduced from Ubbelohde, *Nature*, 1952, **169**, 832.]

A somewhat crude treatment of a phase transformation with coexistence

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[66] Ubbelohde, *Nature*, 1952, **169**, 832.

has been developed for the case of ammonium chloride by Dinichert,[44] based on a mechanical hypothesis about the uniform distribution of stresses in a single crystal in the transformation region. Dinichert's treatment accounts in general terms for the hysteresis loop, but allowance for thermodynamic as well as mechanical contributions to the pseudo-equilibrium seems essential in a more general theory. Unless the sub-regions are large (comparable in size with the single crystal itself), internal " surface energy " at boundaries between sub-regions of structures 1 and 2 may make contributions at least as important as tension and compression energy. Precision *X*-ray studies of the various kinds of lattice change and distortion during transition should throw further light on this point.

Future Work on Phase Transformations in Solids.—It should be clear that provided a sufficient precision of observation can be achieved in work on transformations in solids, great clarification at least of the problems involved can ensue when structural considerations are combined with the requirements of thermodynamics. Work on single crystals practically always throws new light on these problems, complementary to that obtained from work on polycrystalline samples. This is illustrated, for example, by the introduction of the concepts of coexistence of structures in a hybrid single crystal, of the degree of persistence of axes of a single crystal in a cyclic transformation, and of the strain and internal-energy contributions to the free energy of alternative structures, especially when they coexist in a hybrid single crystal around the transformation temperature. Further work will show how far these and related concepts are applicable quite generally to the very wide diversity of transformations in solids.