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## Early Cases of Reentrant Behaviour

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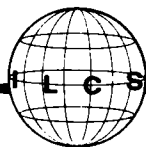
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# Liquid Crystals

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**TODAY**

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## Early Cases of Reentrant Behaviour

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### Introduction

Reentrant behaviour of phase transitions means that by continuous change of a variable of state (usually temperature, pressure or concentration) a certain phase disappears during one transition, and reappears in another transition. In liquid crystals, reentrance was first observed in 1975 by Cladis [1] in a two-component system with temperature as a variable.

However, this was not the first case of reentrance in general; there are several much older cases, and the story was already beginning in the 19th century.

In 1887 Amagat [2] investigated the melting temperatures of several inorganic and organic materials under pressures up to 3000 atm. He reported the idea that there could be a critical point of solidification, i.e. with enhanced pressure the melting temperatures increase passing through a maximum, so that at high enough pressure the liquid again is stable.

In 1891 Damien [3] reported his results of the experimental investigation of the melting temperature of several organic compounds and their dependence on pressure up to about 200 bar. He found nonlinear pressure dependences of the melting temperatures, which could be described by a power expansion up to the quadratic term. By extrapolation from the fitted results maximum melting temperatures were predicted at 'critical' pressures between about 83 and 1200 atm. In most cases the extrapolated pressures were too high for an experimental proof, however Damien claimed to have found a melting maximum in naphthylamine at 83.5 atm.

The results of Amagat [2] and Damien [3] have been repeated by several authors, but Heydweiller [4] and Bridgman [5, 6] in critical reviews were able to show that up to quite high pressures in the said materials there is no melting maximum.

### First experimental observations: maxima in transition pressures

Tammann [7] around 1896 had developed a hypothesis which predicted closed curves for the equilibrium between crystals and isotropic liquids, including maxima of the melting temperature at high pressures. In order to support his hypothesis, Tammann performed high pressure investigations on many com-

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pounds, and he showed that in order to explain the results the pressure dependence of the changes of volume and energy at the phase transitions have to be taken in account.

Tammann [8] in 1900 specially investigated the complex phase diagram of water, in the temperature interval down to  $-80^{\circ}\text{C}$  and with pressures up to 3.2 kbar. He found three solid phases, and in the transition between the modifications I–III he presented the first experimental evidence of reentrant behaviour (figure 1). This is, holding the pressure constant at 2.24 kbar, with decreasing temperature ice III is transformed to ice I at about  $-29^{\circ}\text{C}$ , and at about  $-65^{\circ}\text{C}$  ice III again is formed. The volume contraction during the transition ice I–ice III was between  $-30$  and  $-50^{\circ}\text{C}$  about  $-0.193\text{ cm}^3\text{g}^{-1}$ . Using the equation of Clausius and Clapeyron

(continued on page 2)

$$dT/dp = T\Delta V/\Delta H \quad (1)$$

$\Delta H$  = transition enthalpy  $\Delta V$  = transition volume.

Tammann was able to show, that using his experimental transition volume, the transition heat changes its sign from positive to negative values at about  $-43^\circ\text{C}$ . For

$$\Delta H = 0, dT/dp = \infty.$$

In careful investigations, up to high pressures of about 20 kbar, Bridgman

[9] improved and modified the phase diagram, however, he confirmed the reentrant transition ice I-ice III found by Tammann. The transition between ice I-ice II, also claimed to be reentrant by Tammann [8], according to Bridgman [9] is monotonous: the phase diagram is shown in figure 2. In 1903 Tammann [7] reported the phase diagram of phenol and the transition between the two solid modifications of phenol probably is another case of reentrance, comparable to the transition ice I-ice III. Another maximum pressure in a transition curve,

due to a vanishing transition enthalpy, was found by Bridgman [13] in 1916 in benzene.

### Maxima in the transition temperatures

An important old example of reentrance is the melting of Glauber's salt  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , investigated first by Tammann [10] in 1903. In this case the melting temperature with increasing pressure passes a maximum (figure 3). According to the Clausius and Clapeyron equation (1) this

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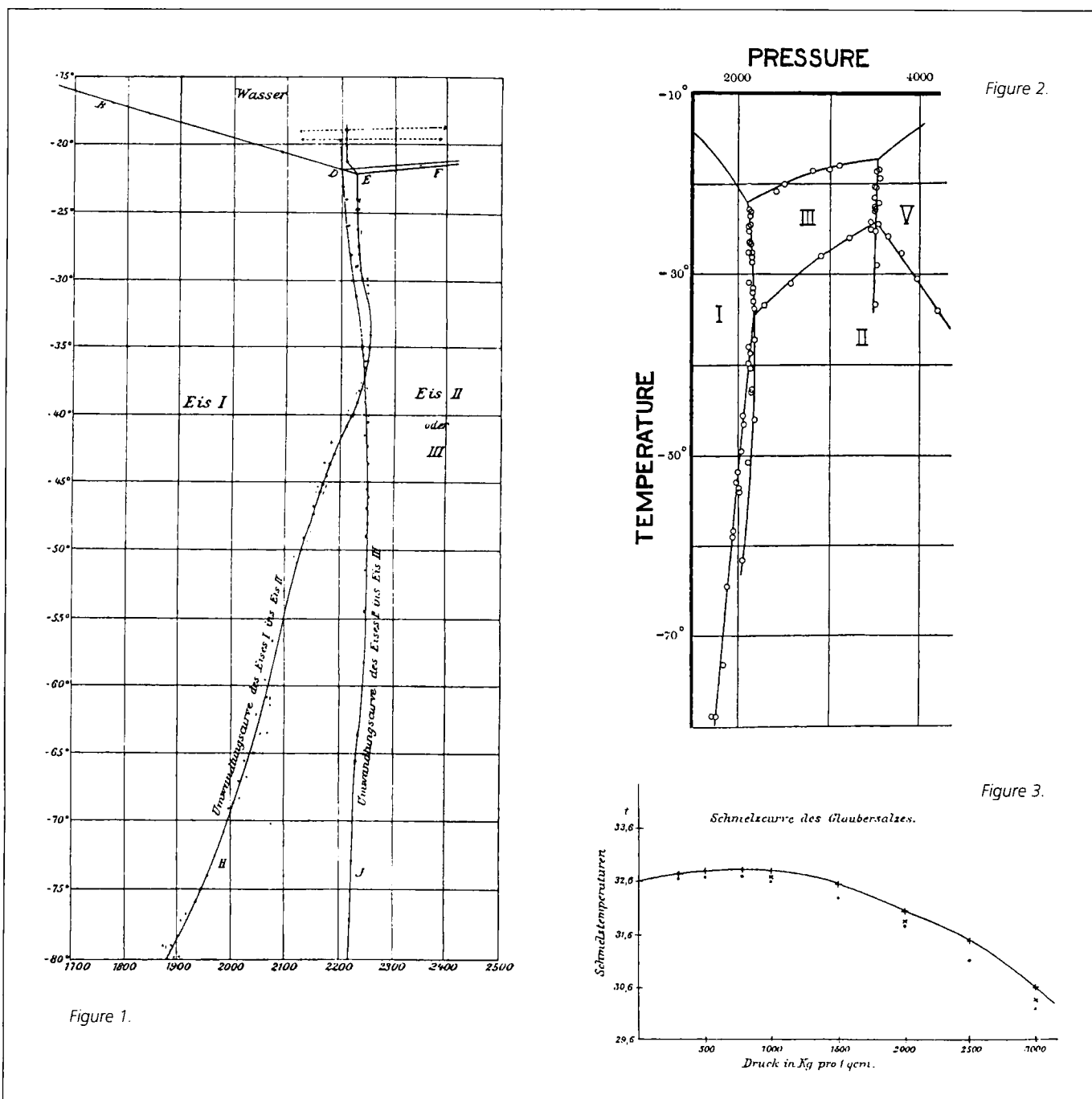


Figure 1. Phase diagram of water from Tammann [8] 1900; Figure 2. Phase diagram of water from Bridgman [9] 1912; Figure 3. Phase diagram of Glauber's salt after Tammann [10].

means that in the maximum, which has been found at a pressure of about 500 bar,  $dT/dp = 0$  and  $\Delta V = 0$ . Tammann considered this to be a proof of his hypothesis about the existence of melting maxima in all substances, and the existence of isotropic liquids at very high pressures.

In the transition curve from red to yellow mercury iodide, Bridgman [11] in 1915 found a maximum in the transition temperature, due to the change of the

sign of the transition volume from positive to negative values with increasing pressure. Bridgman [12] in 1938 reported maximum temperatures for two solid-solid transitions in guanidine sulphate.

Already Tammann [6] knew the thermodynamical conditions for the occurrence of reentrant phase transitions. He showed that in this case the curves of the Gibbs free energy of two coexisting phases, dependent respectively on

temperature and pressure, must have two intersection points (figure 4).

### Reentrance in iron; binary systems

The number of old reentrant examples in pure compounds seems to be very limited. However, in two component systems of iron with several other metals it became known in quite a large number

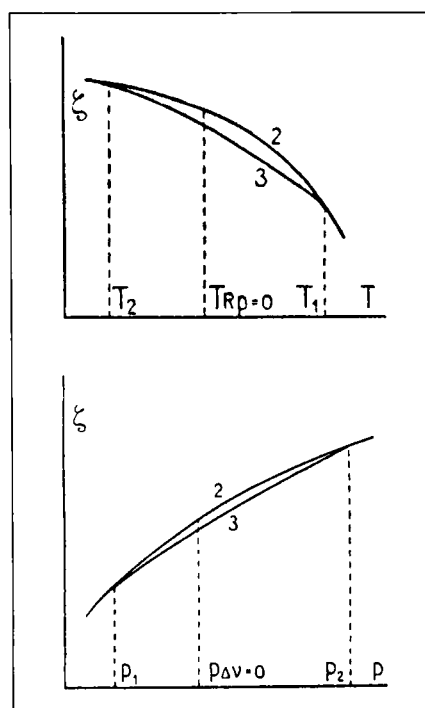


Figure 4. Gibbs free energy depending respectively on the temperature and pressure, after Tammann [6].

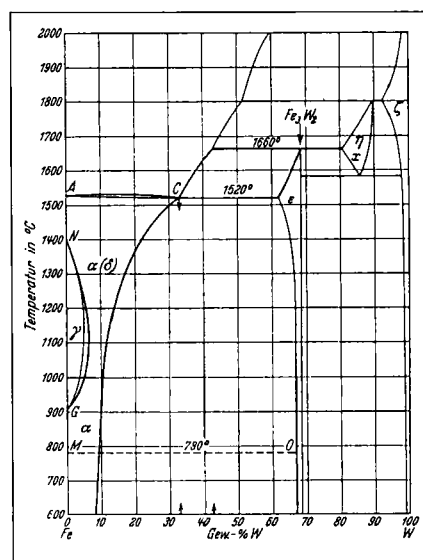


Figure 5. Phase diagram of the system iron-wolfram (from [14], after Takeda [17]).

of cases. In the history of polymorphism of iron many people are involved. Therefore a detailed description is not possible here, and we refer the reader to textbooks of metallography, e.g. the review of Oberhoffer [14]. The polymorphism of iron (table 1) was known from investigations with thermal analysis and other methods, already before the development of X-ray structure investigation methods.

Table 1 Polymorphism of iron

transition temperature (°C)	modification	lattice	lattice constant (Å)
768	α	body centred, cubic ferromagnetic	2.87
906	β	body centred, cubic paramagnetic	2.90
1401	γ	face centred, cubic	3.63–3.68
1528	δ	body centred, cubic	2.93
		liquid	

However, due to the lack of knowledge about the structures of the different phases the reentrant behaviour of β- and δ-iron could not be proved. Around 1921/22 Westgren *et al.* [15, 16] used a new X-ray method and showed the identical structures of α- and β-iron (different only in the magnetic properties) on the one hand, and of the β- and δ-iron on the other hand, the latter two being in reentrant relation (table 1).

The reentrance of iron modifications was strongly confirmed in the years about 1924–1927, when in several binary systems closed loops of mixed crystals connected with the iron γ region were observed. Figure 5 displays a typical example, the system Fe–W (Takeda [17]). Closed γ loops have been found also in the systems Fe–Si (Oberhoffer 1924 [18], Wever 1926 [19]), Fe–V (Maurer 1925 [20]), Fe–P (Haughton 1927 [21]), Fe–Cr (Bain 1926 [22]), Fe–Mo (Sykes 1926 [23]), Fe–Sn (Wever 1926 [24]), Fe–Al (Isawa *et al.* 1927 [25]), Fe–Ti (Roe *et al.* 1925 [26]), Fe–Sb (Wever 1928 [27]), Fe–Be (Wever *et al.* 1929 [28]), Fe–Ta ([14] p. 24).

### Reentrance and liquid crystals

In the literature [29] Valasek [30] is claimed to have found in 1921 the first case of reentrance in phase transitions, however, paper [30] does not deal at all with this phenomenon.

It is worth mentioning that in the old literature the technical term reentrant was never used. According to Cladis [29], Fertig *et al.* [31] in 1977 first used the term 'reentrant' with respect to phase transitions.

In the old literature reentrant cases are rather exotic phenomena, and explanations on a molecular basis could not be

presented. In liquid crystals reentrant cases since their first discovery in 1975 [1] have been reported frequently. The reentrance of nematic, different smectic, columnar and even isotropic phases have been found. In the case of nematic and smectic A phases twofold reentrance became known. In most cases the reentrance occurs at normal pressure and in a convenient temperature range. Therefore liquid crystals are preferred media for the experimental and theoretical study of reentrant phenomena. The reader is referred to the nice reviews of Cladis [30, 32].

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# Important Physical Properties of Smectic Liquid Crystals<sup>1</sup>

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## Introduction

The surface stabilized ferroelectric liquid crystal (SSFLC) device [1] is seen as a promising candidate for future flat panel displays. Its sub-millisecond response time and bistable switching characteristics are attractive features not present in the commonly encountered TN (Twisted Nematic) and STN (Super-Twisted Nematic) displays. A mature ferroelectric display technology has been slow to develop however. One reason for this is the greater difficulties in determining the important parameters which dictate the behaviour of smectic phases. Whilst the viscoelastic equations describing the behaviour of nematics [2] have been extensively studied, the more complicated smectic equations have been explored in only a limited number of instances. The more highly broken symmetry of the smectic C\* phase, deriving from the existence of molecular

layering, results in many new physical phenomena not observable in nematics. For example, complicated layer defects can occur in smectics (by definition an impossibility in nematics); new fluid flow phenomena can occur, related to the anisotropy in flowing across, as opposed to within layers; and the broken symmetry of the Sm-C\* phase requires the introduction of a biaxial dielectric permittivity tensor (rather than the uniaxial nematic tensor). In this article we expand on these examples, highlighting some essential physics for the non-specialist and pointing out some areas of relevance to display technology.

## Alignment in finite thickness samples: chevron states

In an infinite sample, the Sm-A liquid crystal phase is characterized by molecules adopting a layered structure with molecules aligned on average along the layer normal. The Sm-C phase is characterized by molecules everywhere tilted at some equilibrium angle,  $\theta$ , with respect to the layer normal, allowing them to lie anywhere on the surface of a cone of apex  $2\theta$ . Confining a smectic to a finite volume can considerably complicate the layering geometry. In practical devices it is important to understand the layer structure both to optimize device switching times and to minimize the presence of layer defects.

We begin by considering a Sm-A confined between parallel, zero pretilt, rubbed surfaces (figure 1). A transition to the Sm-C requires that the layers adopt a chevron structure in order that molecules can satisfy the mutual constraints of (i) lying at the tilt angle,  $\theta$ , with respect to the layer normal and (ii) maintaining the layer periodicity of the overlying Sm-A phase at the surfaces, which arises as a consequence of molecular adsorption ('surface pinning') in the Sm-A phase [3].

There are two directions in which the chevron apex may point, characterized by opposite sign of the layer tilt angle  $\delta$ . States of positive  $\delta$  are denoted 'C1' and states of negative  $\delta$  'C2' [4]. For a zero pretilt cell these states are clearly equivalent and we can expect both to occur with equal probability. Practically, the existence of both chevron states in a display is undesirable, as a region of C1 meets a region of C2 at a 'zig-zag' defect which scatters light and reduces optical contrast.

The symmetry between the energy of C1 and C2 states can be broken if we introduce surface pretilt, although this results in a further degree of complexity in layer structure. It is illustrative to consider a specific example: consider a cell of finite pretilt,  $\psi$ , in which we constrain molecules to lie at some cone angle  $\theta$  throughout the cell thickness. Furthermore, for concreteness, we suppose that molecules at the surface are constrained