

The Ferro-Electric Phase Transition and Critical Phenomena

[Note: Suitable triglycine sulfate crystals may be available. If not, you will have to "grow" them yourself. This takes a few days.]

1. Introduction

A ferromagnetic substance, such as iron, can carry a permanent magnetization. Above a certain temperature, known as the "Curie point", the magnetization vanishes. This change in magnetic properties is associated with a change in the internal order of the crystal, otherwise known as a **phase transition**. Many condensed matter systems undergo transitions from one phase to another as a function of temperature, pressure, composition and other thermodynamic variables. A familiar example is the solid-liquid melting transition (e.g., ice-water). At the melting point there is a large increase in the entropy, implying a latent heat, and an anomalous behavior in the specific heat.

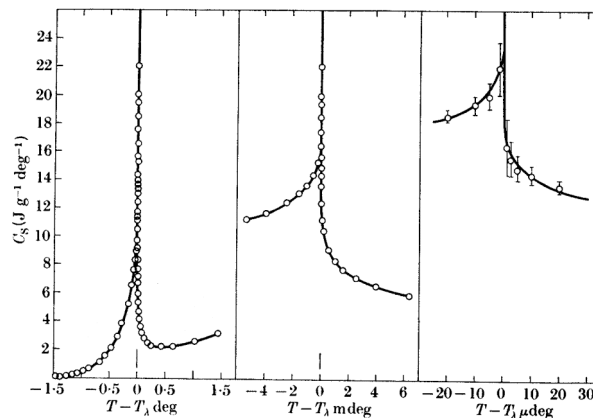


Figure 1 The famous "lambda-point" in the specific heat of ^4He at the superfluid phase transition. (Stanley)

"Ferroelectric" materials are the electrical analogy of ferromagnets: they can carry a permanent electric dipole moment. In this experiment, you will measure the polarization and capacitance of a ferroelectric crystal as a function of temperature, compare them to ferromagnetic behavior, and infer some of the universal characteristics of second-order phase transitions.

2. Phase Transitions and Critical Phenomena

Lev Landau first suggested that the nature of phase transitions is determined by *symmetry principles*. Consider the process known as "melting". The solid phase is a lattice with definite crystal symmetry, while the liquid phase is spherically symmetric. Thus the liquid has no particular symmetry relationship with the solid. The lack of a symmetry relationship between the two phases forbids a *continuous* transition: we have either a solid or a liquid, or a mixture of the two phases in equilibrium,

but there is no point at which the two phases are indistinguishable. These are called *first-order* phase transitions.

On the other hand, if there *is* some identifiable relationship between the two phases in terms of the symmetry elements each possesses, then a continuous transition from one to the other is allowed. A simple example of such a transition is the liquid-vapor transition at the *critical point*. On the critical isotherm, the liquid transforms continuously into a vapor, without a discontinuous change in the volume. At the critical point the two phases are indistinguishable. These are called *second-order* transitions, and are marked, most notably, by the absence of latent heat. For all temperatures below the critical isotherm the transition is discontinuous with a latent heat arising from the discontinuous change in volume. The meaning of the nomenclature about first and second order is discussed in Myers, Appendix 11.4.

The critical point, at which a continuous phase transition occurs, is thus a point of special interest. It has been suggested (Wilson, Fisher, Kadanoff ~1967) that the behavior of a system at its critical point is *universal*: physical properties of the system, such as specific heat or susceptibility, *at* the critical point will not depend on the detailed form of the interactions between individual atoms or molecules. The reason for this is that the transition involves the *co-operative* effect of all the interactions in the system, for instance the alignment of dipoles in a ferromagnet. The important quantities are *long-range* in nature and transcend the details of the short-range interactions as far as the transition is concerned. In this case, the thermodynamic behavior of a superconductor at its critical point (the *sc-normal* transition) should be identical to that of a ferromagnet or even steam at its critical point!

Because of the symmetry restrictions mentioned above, critical points are not very common in solid-state physics. The best-known example is probably the transformation of a ferromagnet to a paramagnetic at higher temperatures. We will briefly review this below. In this experiment, we will look at an *electrical* analog of this transition, one in which a permanent *electric* dipole moment sets in at the phase transition. In this case, the *ferroelectric* ordering of the low temperature state arises from the co-operative alignment of electric dipoles. The ferroelectric transition is relatively easy to measure, and thanks to the universality hypothesis, a convenient laboratory in which to study critical phenomena.

3. Paramagnetism, Ferromagnetism, and the Curie Point

Required reading: Myers, 11.1-11.5, Appendix 11.4.

The study of magnetism in matter is a classic element of solid state physics, and the starting point for any discussion of second-order phase transitions.

A linear paramagnetic substance acquires a magnetization proportional to the applied magnetic field:

$$M = \frac{1}{\mu_0} \chi_m B \quad [1]$$

The susceptibility, χ , determines the strength of the paramagnetic *response*. For non-metals, Curie found the magnetization, and thus the susceptibility, to vary inversely with temperature:

$$M = \frac{1}{\mu_0} \frac{C}{T} B$$

$$\therefore \chi_m = \frac{C}{T}$$
[2]

where C is called the Curie constant. Langevin derived this form by assuming (way before the discovery of spin!) the existence of intrinsic molecular or atomic magnetic moments. Consider a gas of N free magnetic dipoles of strength μ interacting with magnetic field B . If the number of dipoles in each orientation ($\vec{\mu} \cdot \vec{B}$) is weighted by the Boltzmann factor, then, in the limit of small B , the total dipole moment is given by

$$M = \frac{N\mu^2 B}{3kT} \text{ for } \mu B > kT$$
[3]

in agreement with the Curie form. Measurement of the Curie constant yields the intrinsic atomic or molecular moments.

Ferromagnetic substances, like iron, behave like paramagnets at high temperature, but below a certain temperature T_C , acquire a “spontaneous magnetization”. That is, they have a finite value of M , even when $B = 0$. In these materials, long-range interactions between the dipoles create a “mean” internal field that can “bootstrap” an overall dipole alignment. When the temperature is high, the thermal motion of the dipoles prevents this ordering. As the temperature cools, small regions of dipoles become susceptible to fluctuations, which can create small, aligned domains. As cooling continues, these domains are subject to larger aligning fluctuations, the susceptibility grows very large, and at the critical temperature, T_C , a global alignment locks in. In a heuristic interpretation of Eqn. 2, we may say that at the critical temperature, an infinite χ multiplies a zero B to yield finite M .

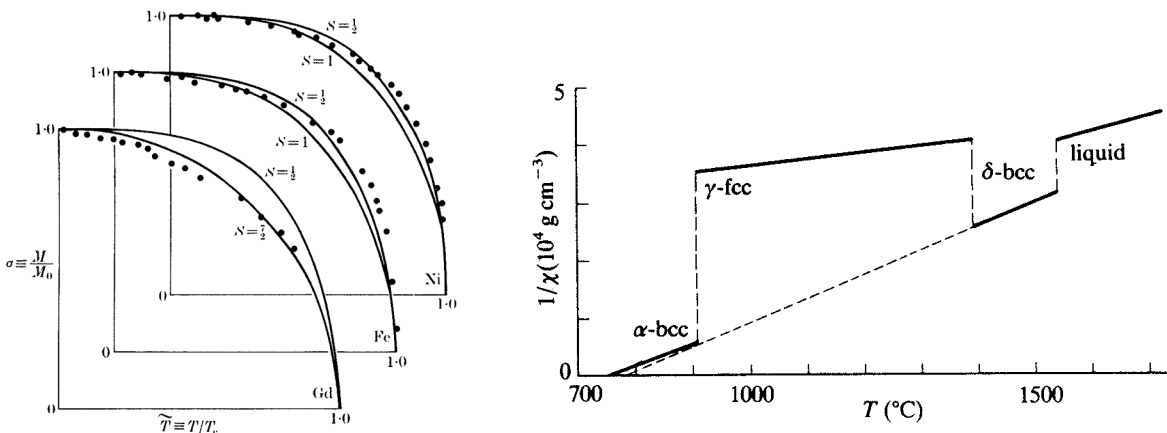


Figure 2 Left: Reduced magnetization vs. reduced temperature for three ferromagnetics with different intrinsic moments, showing universal behavior (Stanley). Right: The inverse magnetic susceptibility vs. temperature in Fe, showing the Curie-Weiss behavior and several Curie points (Myers).

The idea of the “mean field” is actually a simplification of the complex mathematical problem of describing the interacting dipoles. Instead of interacting with each other, the dipoles are assumed to

create a “mean” background field, and interact with that. (See Myers or Stanley.) In the high temperature region, the paramagnetic Curie behavior is modified to the “Curie-Weiss” law

$$\chi_m = \frac{C}{T - T_C} \quad [4]$$

The susceptibility still diverges as $1/T$, but the singularity moves up to T_C , the “Curie temperature”. A permanent magnetization begins to grow at T_C and increases with cooling according to the form shown in Fig. 2-left. Below T_C , the susceptibility continues to follow the Curie-Weiss law. In Fig. 2-right, the inverse of χ is seen to be linear in temperature, but with jumps and slope changes at the transitions.

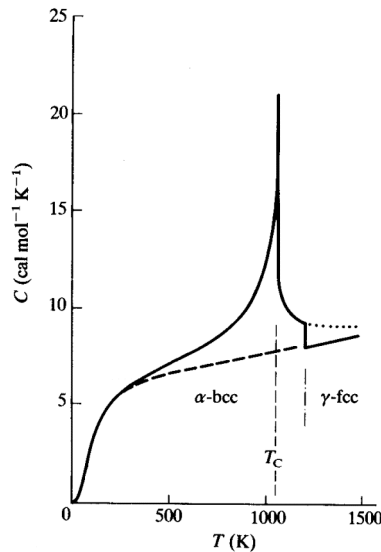


Figure 3 Specific heat of Fe near the Curie point (Myers)

But why is this a **phase transition**? Because, as seen in Fig 3, above, there is a rapid change in the specific heat at T_C , which we usually associate with a “change in state”. However, there is no discontinuous change in the configuration of the system, as in the case of melting or boiling. Instead, there is a change in the amount of **order**: in the magnetic phase, the dipoles are *lined up*. The change in order is accompanied by a change in a symmetry, rotational symmetry that exists in *both phases*. Above T_C there is complete rotational symmetry. Below T_C , the magnetization axis defines a preferred direction in space: there is still rotational symmetry, but there is *less* of it. Landau called this a “phase transition of the second kind”, and invented a powerful technique for studying its critical point behavior. But first, the experiment...

3. Study of the Ferro-Electric Transition in Triglycine Sulfate

Triglycine sulfate (TGS, for short) is a ferroelectric at room temperature and transforms to a ‘para-electric’ state at the critical point, $T_c \approx 49^\circ\text{C}$. A brief summary of the properties and structure of TGS is given in Appendix I. The important point is that TGS is one of the rare solid-state systems that exhibits a continuous phase transition. In Part I, we will measure the *spontaneous polarization* (di-

pole moment/unit volume) that appears at the critical point in TGS and study its temperature dependence in the ferroelectric phase. In Part II, we measure the *electric susceptibility* (via the dielectric constant) of TGS as it changes phase. As you work, keep in mind the analogy to magnetism and the discussion above:

$$\begin{aligned} B &\rightarrow E \\ M &\rightarrow P \\ \chi_M &\rightarrow \chi_E \end{aligned} \quad [5]$$

Part I: Polarization *vs.* Temperature

Use a crystal of TGS (see Appendix I) that has silver paint electrodes on two opposite faces normal to the polar axis. The TGS sample acts as the dielectric in a parallel-plate condenser. The crystal can be heated or cooled slowly through T_c by enclosing it in a heating tape whose temperature can be varied with a variac. The temperature of the sample can be measured with a thermocouple that is placed in thermal (but not electrical) contact with the crystal. The Omega 871A digital thermometer is a hand-held DVM-like meter that reads out the thermocouple voltages and converts to temperatures in degrees.

Note that for this to work the sample and leads must have a very high electrical resistance, so that the charge does not leak off. The leads and crystal should be insulated carefully. (Black electrical tape is good.) Check with an ohmmeter to see that the resistance is >10 Meg.

When the electric dipole moment sets in at T_c charge will begin to accumulate on the crystal surfaces normal to the polar axis, positive charge on one electrode and negative on the other. Since the crystal is an insulator we can assume the charge will not leak away or be shorted out by the crystal. The charge that accumulates (which is just equal and opposite to the spontaneous polarization, P_0 , multiplied by the surface area of one electrode) is measured using a Keithley 610BR electrometer. A reasonable scale to start with is 3×10^{-8} C.

Starting with the crystal at room temperature, measure the charge that accumulates on the sample electrodes as the sample is heated. At room temperature, TGS is in the ferroelectric phase and thus has a fully developed dipole moment. Of course, the sample will be electrically neutral and no charge will be present on the electrodes unless the equilibrium is disturbed, *e.g.*, by heating or squeezing the sample. The former is known as the ‘pyroelectric effect’ and is widely used in heat sensing and infra-red imaging applications. The latter is known as the ‘piezoelectric effect’ and is used to sense acoustic waves and as an ultrasonic transducer.

Use the variac to warm the sample slowly. Start with the variac turned up to about 20 or so and watch the temperature rise. If you raise it too quickly, you will destroy the sample. Measure the charge on the electrodes as the temperature is raised. You should see a dramatic buildup of charge as you pass over the phase transition. Once you are well past the peak, try gradually lowering the temperature. The behavior may not be reproducible due to charge leaking off. Try this several times to find a procedure that gives the best data. When you are finished, make an estimate of the area of the sample electrodes. Try to obtain as many data points as you can in the region of the phase transition, $T_c \pm 15^\circ\text{C}$. Plot a graph of spontaneous polarization, P_0 , as a function of temperature. The units of P_0 are $\mu\text{C}\cdot\text{m}^{-2}$. Plot the same data as a log-log plot: $\ln P_0$ *vs.* $\ln(T_c - T)$, and measure the slope. How does this compare with the theoretical prediction given in Section 4? What

value do you obtain for the saturation spontaneous polarization? If this differs from the value given in Appendix I, why do you think this is so?

Incidentally, the spontaneous polarization of the ferroelectric phase is produced by the displacement of the nitrogen ions from the planes of mirror symmetry m and m' in Figure 3, Appendix I. Given the unit cell dimensions (marked with an arrow in Table I) calculate the displacement of the nitrogen ions needed to give the measured polarization.

Part II: Capacitance *vs.* Temperature

In this part, we study the variation of the electric susceptibility at the critical point. Use the same apparatus as for part I, with a capacitance meter (the Keithley 332 LCZ Meter) instead of the electrometer. The capacitance *vs.* temperature can be converted into the dielectric constant via

$$C = \kappa \epsilon_0 \frac{A}{d} \quad [6]$$

where ϵ_0 is the permittivity of free space (8.85×10^{-12} farad/meter), A is the area of one electrode, and d is the separation of the electrodes. The dielectric constant κ gets you back to the susceptibility.

We do not have the official “4-point” input fixture for the LCZ meter, but the home-made substitute using coaxial cables works remarkably well. The setup and calibration procedure is on page 1-12 of the Keithley manual. Be sure you can use the meter to get an accurate value for a known capacitor before proceeding.

Connect your sample to the LCZ meter. Take data up to $T \approx 80^\circ\text{C}$ on heating then take more data on cooling back to room temperature. Take care not to overheat the sample beyond 85°C . You may not be familiar with the operation of the capacitance bridge, so practice on a few of the standard capacitors provided.

You will find the capacitance varies rapidly in the region of T_c so try to have the temperature changing as slowly as possible in the phase transition region. Try to collect as many data points as possible near T_c .

Plot a graph of K versus $(T-T_c)$ from room temperature to $\sim 120^\circ\text{C}$. Plot the same data in the form $1/K$ vs. $(T-T_c)$. How does the temperature dependence compare with Landau’s prediction (see Section 4)? What ratio of the Curie constants do you obtain?

4: Landau theory of a continuous phase transitions

Required reading: Landau, Chapter 14, Sections 142 and 143.

Landau's theory provides a very elegant technique for predicting the shape of the order parameter and the susceptibilities near the critical point.

a. Assumptions

The basic assumptions of the Landau theory are

1. Continuous phase transitions are driven by the internal "order"
2. The amount of this order is measured by an "order parameter", P , chosen so that

$$\begin{aligned} \eta &= 0 & T > T_c \\ \eta &\neq 0 & T < T_c \end{aligned} \quad [7]$$

For a ferromagnet, $\eta = M$; for a ferroelectric, we might expect $\eta = P$; for a superconductor, η will be related to the Cooper pair density. In particle physics, the masses of the elementary particles are due to a broken symmetry of the weak interaction, and η is the "vacuum expectation value" of the Higgs boson!

3. In the neighborhood of the transition, the thermodynamic potential can be expanded as a Taylor series in the order parameter

b. Setup

The specific thermodynamic potential we are considering is the *Gibbs Free Energy*

$$\phi \equiv G = U - TS - \vec{E} \cdot \vec{P} \quad [8]$$

where U is the internal energy, S is the entropy, P is the polarization, and E is the electric field.

The order parameter is the spontaneous polarization, $\eta = P$.

$$\phi = \phi_0 + 1/2\phi_1 P^2 + 1/4\phi_2 P^4 + \dots \quad [9]$$

For simplicity we neglect higher powers than the fourth – in special cases, e.g. when $\phi_2=0$, higher order terms may be important but we will not consider the possibility here. Note also that only even powers of P appear in the expansion e.g. ϕ is invariant under reversal of the direction of the polarization. This symmetry is required for ferromagnets and ferroelectrics. However, in general both even and odd powers will be present. If one looks further into this, it is seen that odd terms usually lead to discontinuous phase transitions.

b. Treatment of the Critical Point

The condition for stable thermodynamic equilibrium is that ϕ must be a minimum. Thus

$$\left. \frac{\partial \phi}{\partial P} \right)_{P_0} = 0 \quad \text{and} \quad \left. \frac{\partial^2 \phi}{\partial P^2} \right)_{P_0} > 0 \quad [10]$$

where P_0 is the equilibrium value of the order parameter.

According to our definition of ϕ ,

$$\left. \frac{\partial \phi}{\partial P} \right) = E \quad \text{and thus} \quad \frac{\partial^2 \phi}{\partial P^2} = \frac{\partial E}{\partial P} \quad [11]$$

This last quantity is just the inverse dielectric permittivity, $1/K\epsilon_0$ where K is the dielectric constant and ϵ_0 is permittivity of free space (physically, the permittivity is just a response function describing the change in the polarization due to an external electric field).

$$\therefore \frac{\partial^2 \phi}{\partial P^2} = \frac{1}{K\epsilon_0} \quad [12]$$

c. Treatment of the Critical Point (cont'd)

Now we can use equilibrium condition (10) to find the order parameter. The derivative of the potential

$$(\phi_1 + \phi_2 P_o^2) P_o = 0 \quad [13]$$

has two solutions: $P_o=0$ which corresponds to a stable paraelectric phase ($T \geq T_c$) and more interestingly

$$P_o = \sqrt{\frac{-\phi_1}{\phi_2}} \quad [14]$$

corresponding to a *stable* ferroelectric phase ($T < T_c$).

In this case, the non-zero polarization appears even in the absence of an external field (according to equation (11), $E=0$ at equilibrium). This is a somewhat surprising result and it implies that the symmetry of the high temperature phase has been “broken” by the appearance of a polarization. This spontaneous symmetry breaking is a general feature of all phase transitions.

Going back to the form of the potential, we now make one more assumption. We let the coefficient ϕ_1 be temperature dependent, and expand to lowest order:

$$\phi_1 = a(T - T_c) \quad \text{where } a \text{ is a constant.} \quad [15]$$

The polarization in Equation 14 becomes

$$P_o = \left(\frac{a}{\phi_2} \right)^{1/2} (T_c - T)^{1/2} \quad T < T_c \quad [16]$$

and therefore

$$P_o \sim (T_c - T)^{1/2} \quad [17]$$

This is a very important result: the polarization grows like the square root of T below the critical point. If you followed the derivation in Myers, you know that the non-Landau solution is the complicated transcendental expression known as the Brillouin function. *This simpler form for the same quantity, and the elegance of its derivation, illustrates the power of the Landau approach.*

Finally, to find the behavior of the dielectric constant in the region of T_c , as per Eqn. 12, we differentiate the potential twice we get:

$$\left. \frac{\partial^2 \phi}{\partial P^2} \right) P_o = a(T - T_c) + 3\phi_2 P_o^2 = \frac{1}{K\epsilon_o} \quad [18]$$

For $T \geq T_c$, $P_o = 0$, and therefore

$$K\epsilon_o = \frac{1}{a}(T - T_c)^{-1} \text{ for } T \geq T_c \quad [19]$$

(remember the second derivative of ϕ has to be >0 at equilibrium, so this ensures that K is positive definite)

For $T < T_c$, substitute (16), $P_o^2 = (T_c - T) \frac{a}{\phi_2}$ into (18) to get:

$$\begin{aligned} 1 / K\epsilon_o &= a(T - T_c) - 3(T - T_c)a \\ &= 2a(T_c - T) \\ \therefore K\epsilon_o &= \frac{1}{2a}(T_c - T)^{-1} \text{ for } T < T_c \end{aligned} \quad [20]$$

and therefore

$$K\epsilon_o = \frac{1}{2a}(T_c - T)^{-1} \text{ for } T < T_c \quad [21]$$

Thus a plot of the inverse dielectric constant vs. T should reveal linear behavior above and below T_c . The slopes should be in the ratio 2:1. Equations (19) and (21) are equivalent to the Curie-Weiss Law. The Landau theory not only yields the expected form, but makes a prediction for the ratios of the prefactors, or Curie constants!

d. Summary

From simple phenomenological arguments, we have determined the equilibrium behavior of the order parameter (spontaneous polarization) and dielectric constant in the region of the phase transition. Just to complete this discussion of critical phenomena we could write equation (17) and equation (19/21) more generally as:

$$\begin{aligned} P_o &\sim (T_c - T)^\beta \\ K &\sim (T - T_c)^{-\gamma} \end{aligned}$$

β and γ are known as “critical exponents” and describe the singular behavior in the region of T_c . More accurate theories than Landau’s that include the effects of *fluctuations* of the order parameter,

predict $\beta = \frac{1}{3}$ and $\gamma = \frac{4}{3}$ for example. Landau’s neglect of fluctuations puts his theory in the class of so-called “mean-field” theories of phase transitions in which an ordering entity (a spin, dipole moment, displacement, etc.) experiences the average resultant field of all the other similar entities in the system (i.e. the long-range interactions are presumed to inhibit fluctuations of individual entities).

References:**Ferromagnetism:**

H.P. Myers, **Introductory Solid State Physics**. Parts of Chapter 11 have a really nice derivation of the basic features of the ferromagnetic phase transition.

Ferroelectrics:

Lines and Glass, **Introduction to the Physical Principles and Applications of Ferroelectrics**.

Phase transitions and critical phenomena:

S.K. Ma, **Modern Theory of Critical Phenomena**.

H. E. Stanley, **Introduction to Phase Transitions and Critical Phenomena**

Landau theory:

Landau and Lifshitz, **Statistical Physics**, 3rd Edition. If you want to put yourself in the presence of a Master, read Landau)

Appendix I: Some Properties of TGS

Some of the physical properties of TGS are summarized on the following two pages.

The crystals of TGS you are given have been grown from an aqueous solution by slow evaporation. The solubility curve that makes this possible is shown in Figure 1. The morphology of the crystals is shown in Figure 2. The crystal structure is complex and has fairly low symmetry (monoclinic). The mechanism by which the spontaneous dipole moment is created is also complex and is not yet fully understood. However, crudely speaking, the glycine molecule I in Figure 3 on average lies on a plane of mirror symmetry in the structure at $T \geq T_c$ and there is no net dipole moment. We say the structure is “centrosymmetric” in its high-temperature phase. For $T < T_c$ on the other hand, the nitrogen atoms in the glycine molecules are found to be displaced to the left (or right) of the mirror plane, along the polar axis b . Thus a dipole moment is set up in each unit cell. The co-operative displacement of all such nitrogen ions in the sample thus produces a macroscopic dipole moment in much the same way that unpaired spins co-operatively align to create a magnetic moment in e.g. iron.

28 TGS ((NH ₂ CH ₂ COOH) ₃ · H ₂ SO ₄) family																	
28A Pure compounds																	
Nr. 28A-1 (NH ₂ CH ₂ COOH) ₃ · H ₂ SO ₄ , Tri-glycine sulfate (TGS) and (ND ₂ CD ₂ COOD) ₃ · D ₂ SO ₄ , Deuterated tri-glycine sulfate																	
Quantities of (ND ₂ CD ₂ COOD) ₃ · D ₂ SO ₄ are given in brackets as [D:]																	
1a	Ferroelectric activity in TGS was discovered by MATTHIAS et al. in 1956.	56M1															
b	<table border="1"> <thead> <tr> <th>phase</th> <th>II</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>state</td> <td>F</td> <td>P</td> </tr> <tr> <td>crystal system</td> <td>monoclinic</td> <td>monoclinic</td> </tr> <tr> <td>space group</td> <td>P2₁-C_{2h}^{2a})</td> <td>P2₁/m-C_{2h}^{2a})</td> </tr> <tr> <td>θ</td> <td colspan="2">49.42^b) °C [D: 60 °C⁹]</td> </tr> </tbody> </table> <p> $P_s \parallel [010]$. $\rho = 1.69 \cdot 10^3 \text{ kg m}^{-3}$ at RT. $a = 9.15 \text{ \AA}$, $b = 12.69 \text{ \AA}$, $c = 5.73 \text{ \AA}$, $\beta = 105^\circ 40'$ at RT. HOSHINO et al. selected another axial system: $a' = 9.41 \text{ \AA}$, $b' = 12.64 \text{ \AA}$, $c' = 5.73 \text{ \AA}$, $\beta = 110^\circ 23'$ at RT. They are related to those given above by $a' = a + c$, $b' = -b$, $c' = -c$. In the following tables and figures, Wood's axial system will be used without any special reference. Colorless. Transparent. Cleavage plane: (010). </p>	phase	II	I	state	F	P	crystal system	monoclinic	monoclinic	space group	P2 ₁ -C _{2h} ^{2a})	P2 ₁ /m-C _{2h} ^{2a})	θ	49.42 ^b) °C [D: 60 °C ⁹]		56M1 a) 57W3 57P3 b) 66G3 c) 61S10 57W3 57V3 59H6
phase	II	I															
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crystal system	monoclinic	monoclinic															
space group	P2 ₁ -C _{2h} ^{2a})	P2 ₁ /m-C _{2h} ^{2a})															
θ	49.42 ^b) °C [D: 60 °C ⁹]																
2a	Crystal growth Solution method (solvent H ₂ O); evaporation, cooling method from aqueous solution. Solubility in H ₂ O: Fig. 1482.	66K10, 58N1															
b	Crystal form: Fig. 1483 ... 1485.																
3	Z = 2 in phases I and II. Positional and temperature parameters: Tab. 251, 252. Bond lengths and bond angles: Tab. 253; Fig. 1487, 1488. Projection of crystal structure: Fig. 1486.																
4	Thermal expansion: Fig. 1489 ... 1491.																
5a	Dielectric constants: Fig. 1492 ... 1494. $K = 43$ (T = 300K) $\kappa_p = C/(T - \Theta_p)$, $T > \Theta_{II-I}$, where $C = 3.56 \cdot 10^4 \text{ K}$, $\Theta_p = 49.42 \text{ C}$. [D: $C = 1.9 \cdot 10^3 \text{ K}$, $\Theta_p = 59.5 \text{ °C}$.] Effect of pressure: Fig. 1495, 1496. Dielectric dispersion: Fig. 1497 ... 1499.	66G3 61S10															
b	Non linear dielectric properties: Fig. 1500 ... 1505. $\xi = 6.5 \cdot 10^{11} \text{ J m}^5 \text{ C}^{-4}$, $\zeta = 3.7 \cdot 10^{14} \text{ J m}^9 \text{ C}^{-6}$.	58T4															
d	Spontaneous polarization and coercive field: Fig. 1506 ... 1509. $P_0 = 2.8 \mu\text{C cm}^{-2}$ Pyroelectricity: Fig. 1510. Electrocaloric effect: Fig. 1511 ... 1513.																
6a	Specific heat: Fig. 1514, 1515. Transition heat and transition entropy: $\Delta Q_m = 150 \text{ cal mol}^{-1}$, $\Delta S_m = 0.48 \text{ cal °K}^{-1} \text{ mol}^{-1}$ for transition II → I.	57H2															
7a	Piezoelectricity: Fig. 1516 ... 1519.																
b	Electrostriction: Fig. 1520; Tab. 254.																
8a	Elastic compliances and stiffnesses: Fig. 1521.																
b	Ultrasonic absorption: Fig. 1522 ... 1528; Tab. 255.																
9a	Refractive indices: Fig. 1529 ... 1533. Reflectivity in far infrared region: Fig. 1534, 1535.																
b	Electrooptic effect: Fig. 1536, 1537.																
c	Brillouin scattering: Fig. 1538.																
10	Electrical conductivity: Fig. 1539, 1540; Tab. 256.																
12a	NMR: Fig. 1541 ... 1543; Tab. 257, 258.																
b	ESR: Tab. 259																
13b	Diffuse X-ray scattering: Fig. 1544 ... 1547.																

From: Landholt-Bornstein Tables of Physical Properties (Band III: Ferroelectrics)

TGS

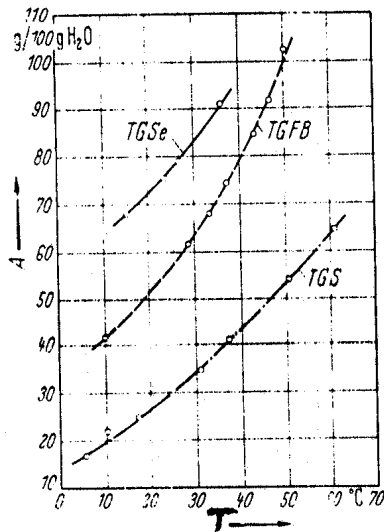


Figure 1. Solubility of TDC in water at various temperatures. TGS crystals are grown by evaporating or cooling a saturated solution.

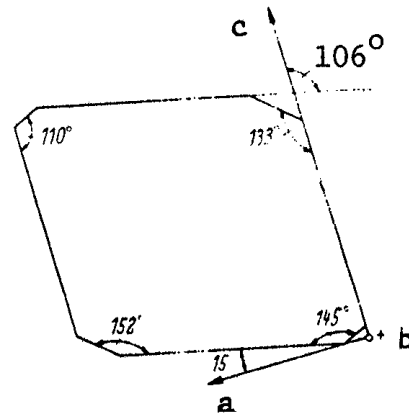
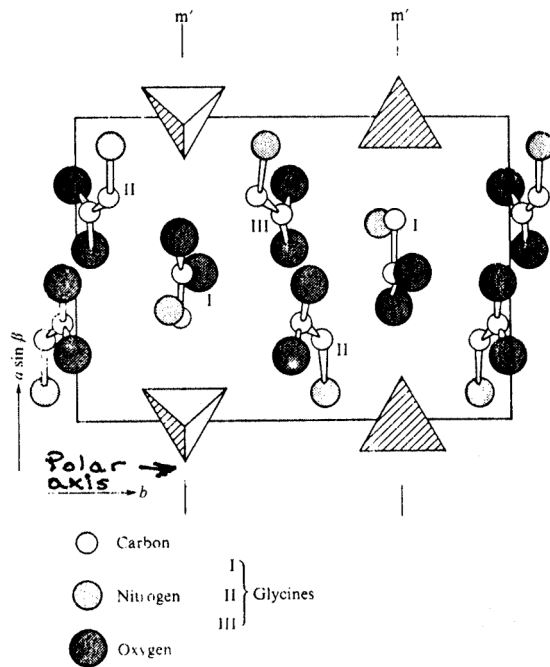
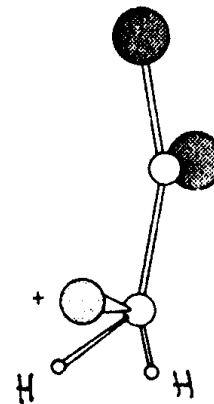


Figure 2. Usual growth habit of TGS crystals. The polar axis is normal to the page.



(a)



(b)

Figure 3. View along the c -axis of the structure of TGS (after Hoshino, Okaya and Pepinsky, 1959; Itoh and Mitsui 1973) showing the three glycine groups I, II, and III. The sulphate ions are shown as tetrahedral. m and m' are mirror planes in the high temperature phase.