

# 1. Introduction: Surfaces and interfaces in potential applications

*In a very real way, then, materials are a reflection of who we are, a multi-scale expression of our human need and desires.* - Mark Miodownik [1]

The global search for more powerful electronic devices, in order to solve increasingly complex problems, is in large parts enabled by miniaturisation of electronic components [2, 3]. The most recent case is found in the production of transistors on semiconducting chips, where ultraviolet light as well as soft and hard X-rays are deployed in lithography techniques [4, 5]. Concepts and ideas fuelling this development are reported up to 2015 in the *international technology roadmap for semiconductors* (ITRS) [6].

After 2015, the ITRS was replaced by the *international roadmap for devices and systems* which is published annually to this date [7]. In recent years the focus broadened from a continuation of the miniaturisation of complementary metal-oxide-semiconductors (CMOS) components, equalling a *more Moore* approach, to explore *more than Moore* and *beyond CMOS* pathways. While the former aims to expand the existing CMOS technology by integrating sensors and actuators into microelectronics, therefore creating monolithic hybrid devices [8], the latter focusses on devices exceeding CMOS technology, enabling current control based on fundamentally new principles of operation.

Under the scope of beyond CMOS, Mott based devices are introduced, such as Mott based field effect transistors (MottFET) and Mott memory devices [7]. The advantage of such Mott insulators in comparison to semiconductors is the reduced energy consumption during operation [9, 10]. In Mott insulators the electrons are mainly localised due to strong Coulomb repulsion and their motion is restricted to hopping events [11, 12]. When the rate of hopping increases and the corresponding kinetic energy term overcomes the Coulomb repulsion, an insulator-to-metal transition takes place, which can be induced by various means e.g. temperature, electric-field, hydrostatic pressure, chemical pressure and strain [12–16].

It does not come as a surprise that such a versatile material class may offer a platform

for electronics, beyond CMOS technology, the Mottronics [17–19]. The fast operation speed in Mott insulators, the switching between the insulating and the metallic state can be achieved on the sub-nanosecond time scale in a robust manner [20]. This allows many repetitions of e.g. writing and reading information in memory devices or opening and closing conducting channels in transistors [9, 10]. Especially these Mott memories are of interest for future applications, for the aforementioned reasons. They consist of a metal-insulator-metal structure, with the insulator showing a high electron correlation [20, 21]. The transition between insulating and metallic state is of first order nature, meaning a sharp transition that can be excited by an external electric field, allowing full control of the system [11, 22]. In order to achieve this, a thorough study of the transition and possible materials is needed.

Lacunar spinels represent a novel class of Mott insulators, the so-called cluster Mott insulators [23], where the electrons are localised on molecular clusters instead of atomic sites.  $\text{GaV}_4\text{S}_8$ , the system subject of this thesis, is a lacunar spinel with a structural transition temperature around 42 K, minimising the effect of thermal fluctuations. It is found that the resistive switching is induced with less than 10 kV/cm making it highly susceptible to electric fields [20, 24]. The strong electric fields are shown to close the correlation gap and drive the system metallic, causing an avalanche break down of the Mott gap [25]. Further, the transition was found to be independent of temperature, preventing a transition induced by Joule heating as is found in Vanadium oxides, a archetypical class of Mott insulators [13, 20]. In addition it is found for Mott insulators that the insulator to metal transition can be induced by pressure [13, 26].

This thesis investigates the conductive features found on the surface of  $\text{GaV}_4\text{S}_8$  and explores their origin [27, 28]. This is achieved by a combination of surface sensitive scanning probe techniques utilising electrical measurements as well as polar ones. Point I(V) spectroscopy is deployed in order to gain a better understanding of the current response of the different features by fitting the data to commonly used models of conductivity.

## 2. Ferroelectric materials and their nanoscopic features

In this chapter, the basics of ferroelectric materials as well as their phase transitions and properties are discussed in order to lay the groundwork for the experimental section.

Ferroelectric materials exhibit a macroscopic polarisation due to the uniform order of local electric dipoles. This ferroelectric polarisation can be switched by external electric fields, driving the system from one polar state to another energetically equivalent polar state.

### 2.1. Symmetry in solids and phase transitions

The concept of symmetry and its significance in solid materials is introduced here with the example of water in its different phases (vapour, liquid and solid) [12, 29]. In the vapour phase water molecules spread over a large volume with attraction between individual molecules which leads to enhanced density fluctuations. On the microscopic scale, the density of these molecules will spontaneously vary while on the average it stays the same. Upon reducing the average kinetic energy of the water molecules, e.g. by cooling down the system a transition to the liquid phase takes place. The reduction of the kinetic energy increases the density and in turn leads to more interaction between the molecules via attractive hydrogen bonds and to the gas-liquid transition.

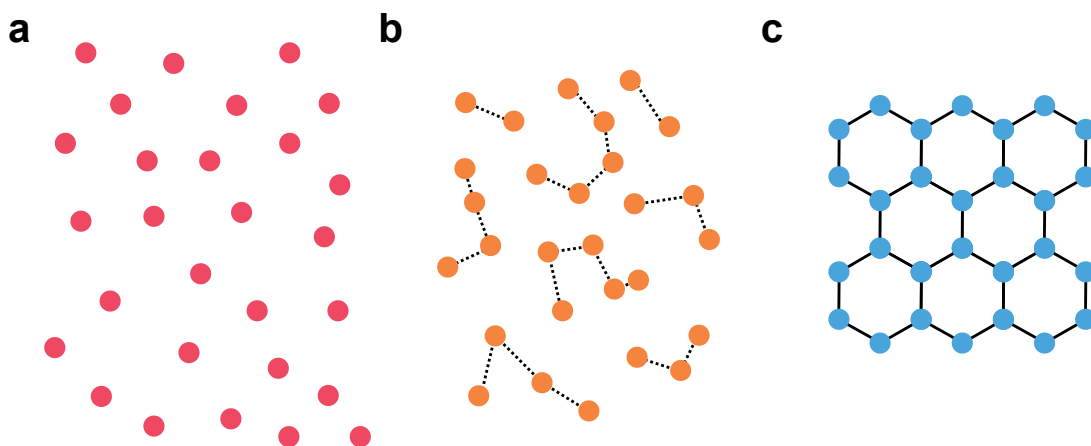
Both the vapour and the liquid phase have full rotational and translational symmetry. The major differences between the two phases are the increased density and lesser compressibility in the liquid phase. The lack of compressibility arises from the distance between molecule being already small due to attractive and repulsive forces. Further cooling down the water leads to a liquid-solid transition, where the short-ranged interactions lead to a long-ranged order in the solid phase. This solidification process leads to the loss of full rotational and translational symmetry. The ice is not a perfectly ordered crystal, but finite remanent entropy due to unavoidable disorder of hydrogen bonds. Although the material loses the high

## 2. Ferroelectric materials and their nanoscopic features

---

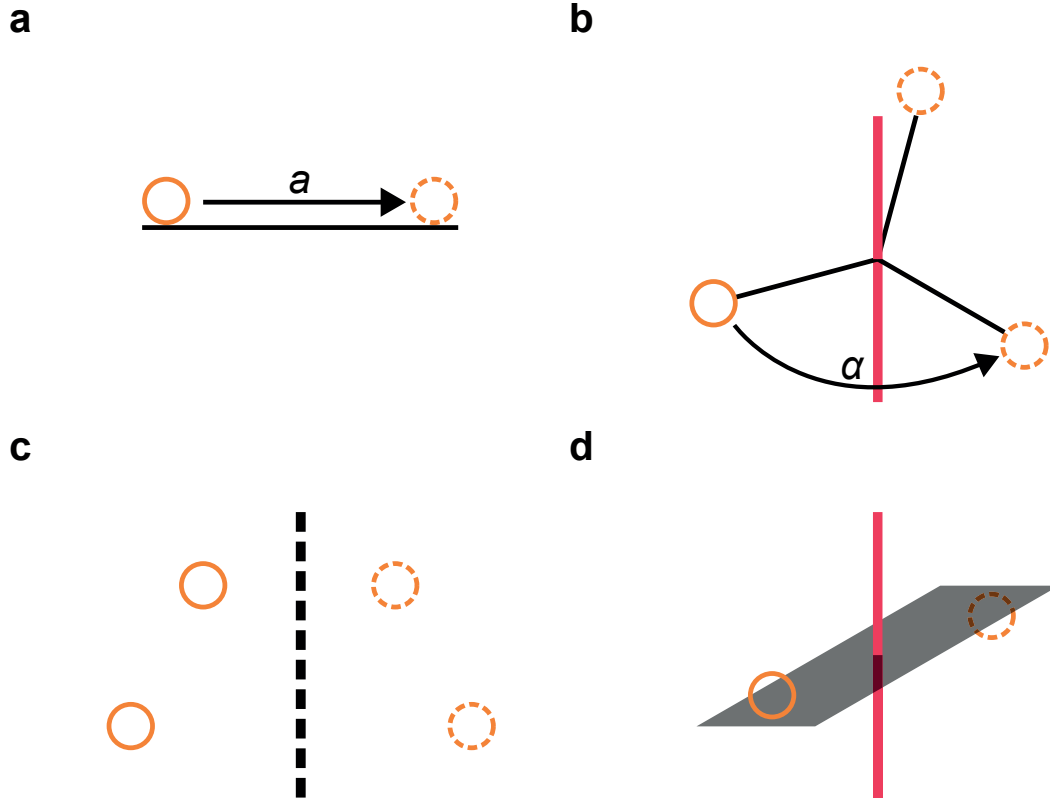
degree of symmetry it gains new properties, e.g. being hard and resistive to shearing. Note, compressing ice induces a solid-liquid transition, which is the reason why skiing is possible. Water can also solidify in completely regular crystalline forms, in fact, change from the standard hexagonal symmetry into twenty different forms under pressure and at different temperatures [30].

Similar processes like in ice take place in other solid materials, meaning a change in structure due to surrounding conditions, e.g. temperature, pressure etc. can lead to new phases and new functionalities. One can then utilise these novel properties for different applications.



**Figure 2.1.:** Schematic of water molecules in the vapour (a), liquid (b) and solid phase (c). The dotted lines represent hydrogen bonds and the colour of the molecules resembles the temperature from hot (red) to cold (blue). Recreated from [12].

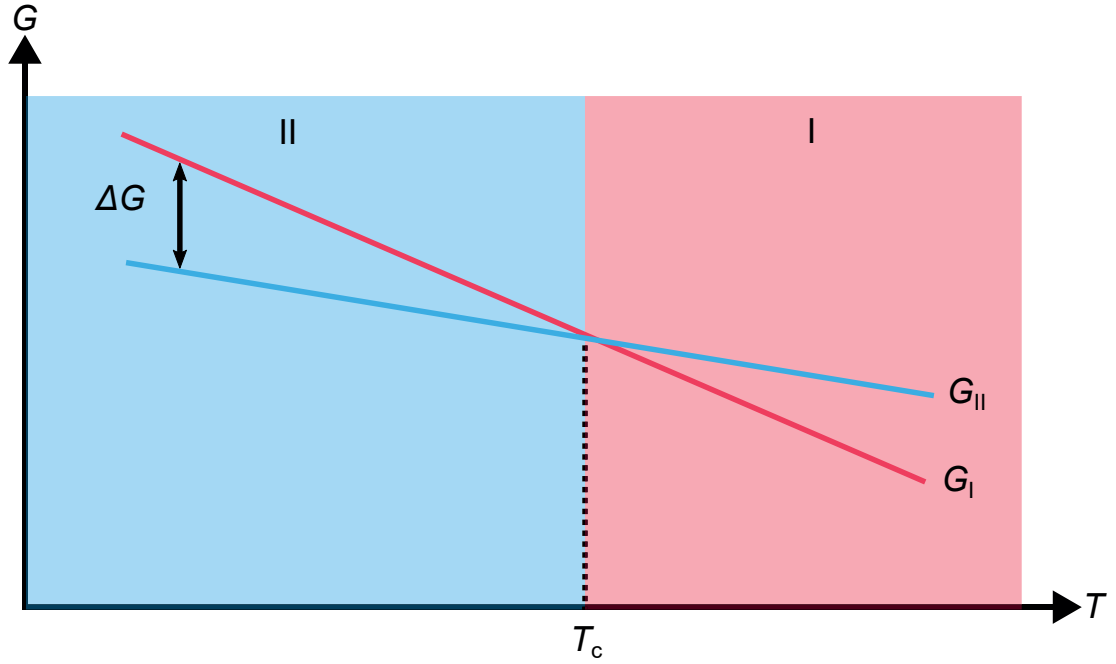
The symmetry information covers different symmetry operations, including translational, rotational, mirror and inversion symmetry [31]. The translational symmetry describes the operation, that one can take the atoms of a crystal and move (translate) them in one or more directions by a set distance. Afterwards the arrangement would be the same as before the operation, giving it an invariance to translation. The relation between symmetry and invariance is known as Noethers theorem [32]. Furthermore, the crystal system may possess rotational symmetry, meaning that one can rotate the atom by a set degree around one axis and be in a equivalent position. For the mirror symmetry, one imagines a mirror in a plane reflecting the position of the atoms of one side to the other. The last symmetry operation, the inversion is a combination of rotation and mirror. Here, a rotation by  $180^\circ$  is followed by a reflection on a plane, which stands perpendicular to the rotational axis.



**Figure 2.2.:** Schematic depicting the four different symmetry operations, translation (a), rotation (b), mirror (c) and inversion (d). Based on information from references [33, 34].

The sum of symmetry operations in a crystalline system define it well and are contained in the crystallographic space group, of which 230 exist in total in three dimensions. By taking only the directional symmetries into account, the space groups can be divided into 32 point groups which give the 32 crystal classes [35].

At a given temperature a structure is stable, but this does not mean it is the most stable symmetry at any temperature above or below the defined temperature. A system then undergoes a phase transition, transforming from one state into another. The state with the smallest free energy, in thermodynamic terms, is considered to be stable. A possible scenario depicting this is shown in figure 2.3. At a temperature above  $T_c$  phase I is favoured for it has the lower Gibbs free energy. At the transition temperature a crossing of the two free energies occurs with  $G_{II}$  being in a lower energy state at lower temperatures and therefore more stable [36].



**Figure 2.3.:** Schematic of the Gibbs free energy depending on the temperature for two different phases (I and II) with respective Gibbs free energies ( $G_I$  and  $G_{II}$ ). The energies cross at  $T_c$ , where  $G_I > G_{II}$  favouring phase II in the low temperature range.  $\Delta G$  is a measure of the transition rate between the phases. Recreated from [36].

Describing such a transition in a mathematical way is a rather daunting task, but was nonetheless done by Landau [37]. The key insight is the introduction of an order parameter, a quantity that is zero above the transition but finite below it. This leads to the rise of a property in the low temperature state and the absence of the same in the high temperature state. The rise of order is usually associated with the lowering of symmetry upon the phase transition. These transitions are often continuous or of second order, as the onset of the order parameter increases gradually below the transition temperature. Second order indicates that the derivative of the order parameter with respect to temperature, which is the second derivative of the free energy with respect to the conjugate field and temperature, shows a discontinuity at the transition temperature, while the order parameter itself is a continuous function of the temperature [36].

The concept of a macroscopic symmetry breaking quantity, the order parameter, may be still applicable to first order transitions, where the order parameter shows a discontinuity at the transition temperature.

## 2.2. Ferroics

The symmetry lowering associated with the ordering of a system can lead to domains with different orientation of the order parameter. The domains are energetically equivalent states and can be transformed into one another by the conjugate field, that is the magnetic, electric or mechanical field for ferromagnetic, ferroelectric and ferroelastic order respectively. Adjacent domains, with different orientations of the order parameter, are separated by domain walls. Cycling of the conjugate field between positive and negative values is often accompanied by a hysteresis of the order parameter. Hysteresis refers to a range, where the order parameter is not a single-valued function of the conjugate field. In terms of domains, it is related to the coexistence of different domains, one representing the thermodynamically stable state and the other being a metastable state. In the following, we concentrate on ferroelectric materials and their physical properties.

Going a bit back in time to 1665 where E. Seignette of La Rochelle created Rochelle salt as a mild drug and started the history of ferroelectrics [38]. The ferroelectric properties of that material went undiscovered for quite some time. The brothers J. and P. Curie did an extensive study about the piezoelectric properties of Rochelle salt and several other crystals, however they overlooked the dielectric properties [39]. The term of ferroelectricity was coined by E. Schrödinger in 1912 [40], but only in 1921 J. Valasek showed the reversibility of spontaneous polarisation by the application of an external electric field and fundamentally studied its dielectric properties [41].

With  $\text{KH}_2\text{PO}_4$  a model system of ferroelectricity, in which mobile hydrogen atoms are responsible for the ferroelectric behaviour, was discovered by P. Scherrer and explained by G. Busch [42]. The rather simple structure, in comparison to the complex Rochelle salt with four formula units per unit cell containing 112 atoms, allowed detailed studies and opened the door for synthesising it in industrial standards [35].

Due to the piezoelectric properties, mechanical deformations leading to the formation of an electric field, this material was deployed as sound transducer and submarine detector in the Second World War. In 1941, J. Slater formulated a first model for ferroelectrics, considering the possible orientation of  $(\text{H}_2\text{PO}_4)^-$  units with respect to the hydrogen bonds, allowing a total of six different directions [43]. Up to then the general idea of ferroelectric behaviour is based on hydrogen bonds playing a crucial role. In the 1940s the ceramic  $\text{BaTiO}_3$  is discovered to show large dielectric

## 2. Ferroelectric materials and their nanoscopic features

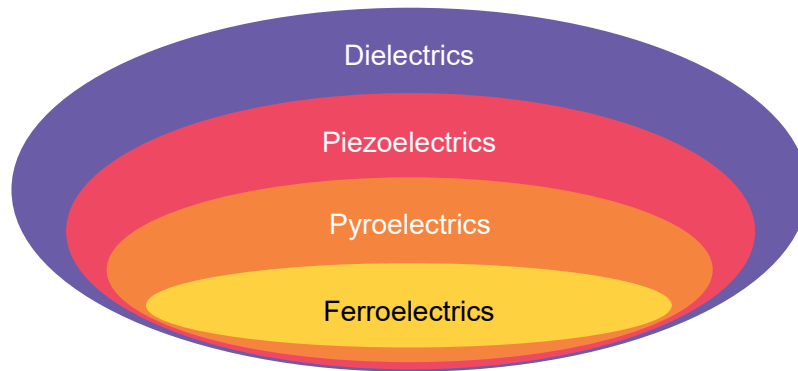
---

constants at room temperature [35]. This first non natural occurring ferroelectric was researched extensively since then [44–48]. The research on this material in return opened the path for a myriad of ferroelectric materials, e.g.  $\text{KNbO}_3$  [49],  $\text{LiNbO}_3$  [50] and  $\text{PbTiO}_3$  [51] and fascinates scientists to this day.

### Ferroelectricity

Ferroelectric materials show an electric dipole moment, even in the absence of an external electric field and are switchable between two or more symmetrically equivalent states. This switching shows a hysteretic behaviour of the polarisation in a external electric field, with the total polarisation being the sum of all electric dipole moments in a studied volume [31]. A dipole moment is a separation of charges in a unit. This unit can be a single molecule, e.g. the separation of electrons between oxygen and hydrogen in a water molecule or movement of ion cores in a crystalline unit cell. In a crystalline unit cell, the charge is overall balanced, i.e. the unit cell is charge neutral despite its finite dipole moment.

Ferroelectric polarisation is only compatible with certain crystal symmetries. In materials with spatial inversion symmetry, the polarisation is forbidden. If a crystal has a two-, three-, four-, or six-fold rotation axis, finite polarisation is only possible along this axis. If there is a mirror plane, the polarisation must always be parallel to this plane. Due to these symmetry restrictions, ferro- or pyroelectricity is only possible in ten out of 32 crystal classes. The historical term dielectrics refers to all



**Figure 2.4.:** Schematic showing the relation of different material families to each other. Recreated from [52].

non-metallic materials, which can be polarised by external electric fields. A still large sub-class is the family of piezoelectrics, that are materials without spatial inversion



symmetry, where electric fields lead to mechanical deformation. A further sub-class is pyroelectrics, which exhibit finite electric polarisation often from their growth. This polarisation is usually temperature-dependent but cannot be reversed by external electric fields. Finally, the family of ferroelectrics refers to such polar materials, where the polarisation can be controlled by electric fields.

### Landau theory for ferroelectric phase transitions

The Landau theory for ferromagnetic phase transitions is a formal thermodynamic description to explain the transition of ferroics by the expansion of the free energy as a function of the polarisation [37]. It was later expanded by A. Devonshire for ferroelectric phase transitions [53]. In the following the Landau free energy describing a para- to ferroelectric transition in a system, where the polarisation has only one component, i.e. it is parallel or antiparallel to a given axis is discussed. Starting with the Gibbs free energy, extended by an external electric field, as shown in equation 2.1. Only the even powers are taken into account, since the form of the free energy must be unchanged by any symmetry of the disordered phase, i.e. must stay invariant upon inversion. The powers are only considered up to the 6th order, if the order parameter is small enough, to further simplify the equation [31, 36, 37]:

$$F = H - TS - EP, \quad (2.1)$$

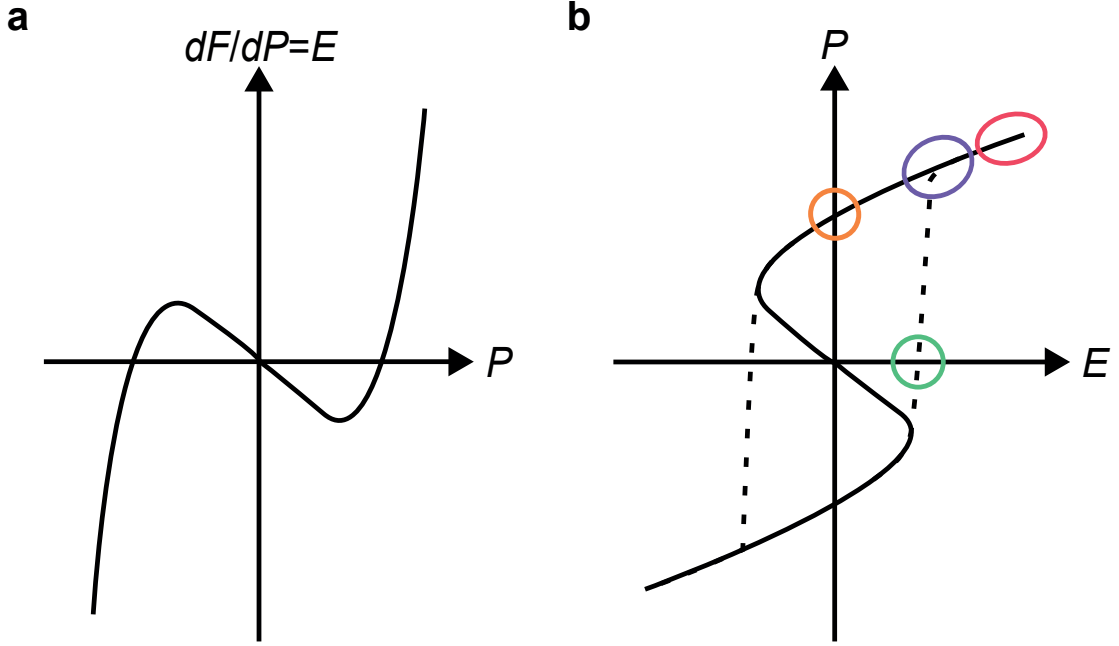
$$F = F_0 + \alpha P + \frac{\alpha}{2}P^2 + \frac{\beta}{3}P^3 + \frac{\beta}{4}P^4 + \frac{\gamma}{5}P^5 + \frac{\gamma}{6}P^6 - EP, \quad (2.2)$$

$$F = F_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 - EP. \quad (2.3)$$

The stability condition, that requires a minimum of the free energy, reads as follows:

$$\frac{\partial F}{\partial P} = 0 = \alpha P + \beta P^3 + \gamma P^5 - E, \quad (2.4)$$

$$E = \alpha P + \beta P^3 + \gamma P^5. \quad (2.5)$$



**Figure 2.5.:** **a** Illustration of the electric field plotted over the polarisation from equation 2.5. **b** Schematic of the polarisation plotted over the electric field (thick line) with the hysteretic behaviour of a prototypic ferroelectric (dashed line). Characteristic points include remanent polarisation (orange), coercive electric field (green), saturation polarisation (red) and a second change in the slope (purple). The schematic is adapted from [54] and based on information from [55].

This form is the Maxwell field, orientated parallel to  $P$ . If we assume no external electric field ( $E = 0$ ), we get the following equation:

$$(\alpha + \beta P^2 + \gamma P^4)P = 0, \quad (2.6)$$

with  $P = 0$  and  $\alpha + \beta P^2 + \gamma P^4 = 0$  as possible solutions. While the first describes the paraelectric state, for no net polarisation exists in the system, the latter is the condition for minimum free energy in the ferroelectric state. To obtain the ferroelectric phase,  $\alpha$  must pass through zero, therefore giving:

$$\begin{aligned} \alpha &= \alpha_0(T - T_0) \\ \alpha &> 0, \text{ for } T > T_0 \\ \alpha &< 0, \text{ for } T < T_0 \end{aligned} \quad (2.7)$$

with  $T_0$  being the phase transition temperature.

Two different scenarios result if we consider the sign of  $\beta$ . For this the polarisation