

# Saturation Effects in Ferroelectric and Ferroelastic Phase Transitions

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Received August 8, 2003; in final form January 5, 2004

*The saturation of order parameters in phase transitions at low temperatures can arise from two mechanisms; true saturation of the order parameter, and quantum mechanical saturation. The effect of these two processes on graphs of order parameter versus temperature and on phase diagrams in a range of systems is described.*

**Keywords** Phase transitions; thermodynamics

61.50.Ks Crystallographic aspects of phase transformations; pressure effects

81.30.Dz Phase diagrams of other materials

81.30.Hd Constant-composition solid-solid phase transformations: polymorphic, massive, and order-disorder

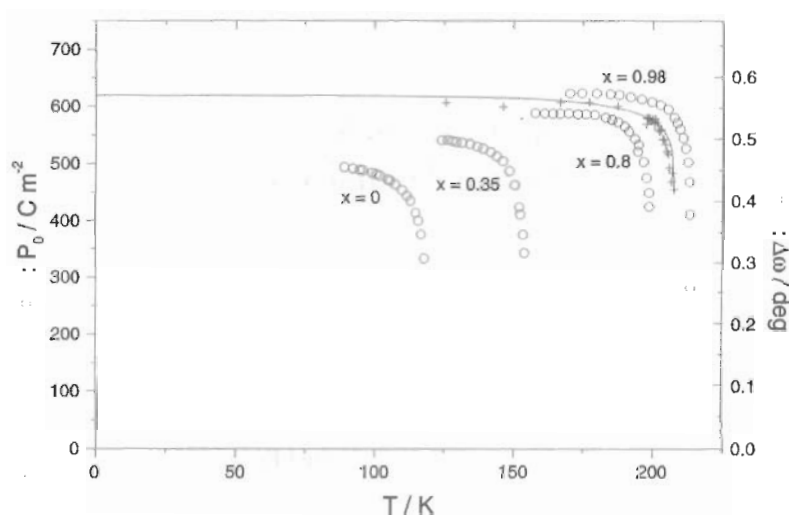
77.80.Bh Ferroelectricity: Phase transitions and Curie point

## Introduction

The thermodynamic behaviour of systems at low temperature is complicated by the constraint of the third law of thermodynamics, that entropy changes vanish as absolute zero temperature is approached. One consequence of this is that the order parameters of phase transitions tend to a finite limit at low temperatures. This saturation can have classical or quantum mechanical origins. In this article, we outline the differences between these types of saturation in ferroelectric and ferroelastic systems, and their effect on the phase diagrams of these materials.

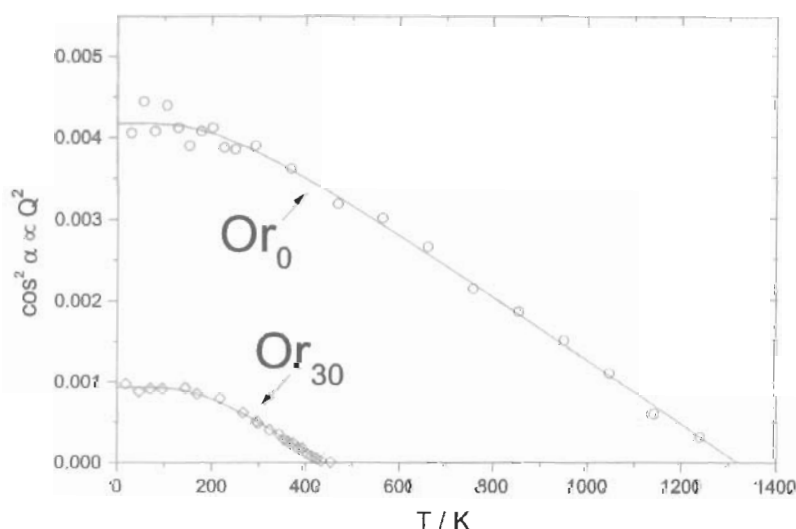
## Mechanisms of Order Parameter Saturation

In phase transitions where the transition mechanism is dominated by an order-disorder process, saturation will occur when the structure becomes completely ordered. A classic example of this saturation is the ordering of dipoles in KDP-type ferroelectrics [1, 2], shown in Fig. 1. This classical saturation of the order parameter is defined by a maximum value of the order parameter. The saturation of these systems is well described, in the mean-field limit, by a free energy function where the entropy is configurational, as in (for example) a Bragg-Williams model [2, 3].



**FIGURE 1** Temperature dependence of the order parameter in  $\text{KH}_{2(1-x)}\text{D}_{2x}\text{PO}_4$ , using two different experimental methods. The open circles show the polarisation data of Samara [1]. The crosses and fit line are the twin angle (spontaneous strain) data and macroscopic model of Hayward et al. [2] for a sample with  $x = 0.82$ . The relative scaling of the two types of data is somewhat arbitrary.

For phase transitions with an inherently displacive mechanism, the absolute maximum value of the order parameter is not a significant consideration. An example is provided by the  $C2/m - C\bar{1}$  phase transition in the mineral anorthoclase. The degree of tilting of the aluminosilicate framework (i.e. the order parameter) may be measured from the spontaneous strain  $e_4$  ( $\propto Q$ ), as shown in Fig. 2.



**FIGURE 2** Order parameter vs. temperature graphs for two anorthoclase samples;  $\text{Or}_0$  is a pure sodium feldspar, and  $\text{Or}_{30}$  is 30% K, 70% Na feldspar. Some of the data in the  $\text{Or}_{30}$  curve are from Harrison and Salje [4].

Unlike the ferroelectric ordering of dipoles seen in the KDP system, there is no fundamental limit on the magnitude of the tilting undergone by the framework. Instead, the saturation is characterised by a temperature: in the case of the anorthoclase system, the order parameter is independent of temperature below 135 K. In the notation of Pérez-Mato and Salje [5], this corresponds to a saturation temperature  $\theta_S = 270$  K.

In this case, the saturation has a quantum mechanical origin; as the relevant vibrational modes approach their ground state, it becomes impossible to reduce the overall free energy of the system by changes in the order parameter. The saturation temperature  $\theta_S$  therefore depends on the frequency of the mode associated with the phase transition.

## Saturation Effects in Phase Diagrams

Phase transitions often show a strong dependence on secondary variables such as chemical composition, pressure or electrical fields. The effects of solid solution on phase transitions have been reviewed by Heaney [6]. In the displacive limit, these variables are easily incorporated within a thermodynamic model of the sort examined in [7];

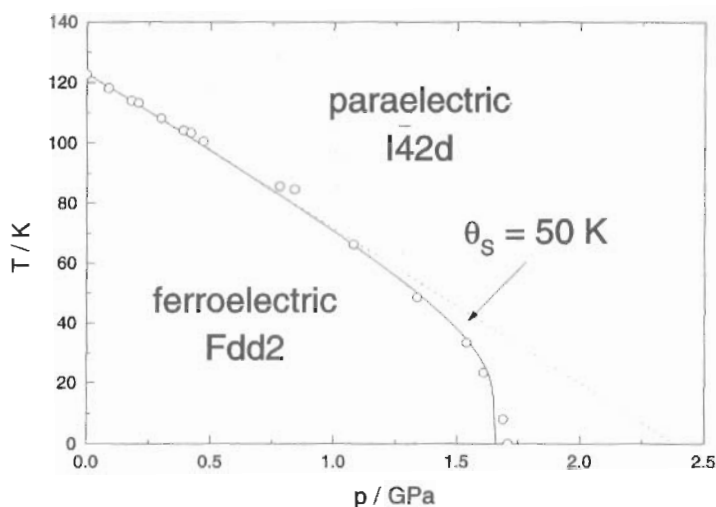
$$G = \frac{A}{2} \left( \theta_S \coth \frac{\theta_S}{T} - \theta_S \coth \frac{\theta_S}{T_C} \right) + \frac{B}{4} Q^4 + \dots + G(\text{coupling}), \quad (1)$$

where the exact form of  $G(\text{coupling})$  depends on the symmetry of the interaction between the secondary variable and the order parameter. For instance, in a proper ferroelastic (such as anorthoclase), the coupling term due to chemical doping has the form  $\lambda x Q^2$ , where  $\lambda$  is a coupling constant and  $x$  is the dopant fraction.

Given Eq. (1), it is straightforward to calculate the transition temperature as a function of  $x$ . As may be imagined from consideration of Fig. 2 above,  $T_C(x)$  will be linear in  $x$  at high temperatures, and then fall quite rapidly once  $T_C(x)$  approaches  $\theta_S$ . The phase diagram will have a similar form to the  $Q^n(T)$  graph (for whatever  $n$  gives linear classical behaviour) [5]. This result is in agreement with quantum mechanical calculations [8].

A similar argument does not apply directly to order-disorder systems; as Fig. 1 shows, the observed saturation of the order parameter is not driven by quantum mechanical effects. However, we still expect quantum mechanical saturation to occur, if the secondary variable depresses the order parameter enough. For a phase transition which is second order throughout, the phase diagram shows identical saturation behaviour to the displacive case [5]. As an example, Fig. 3 shows the  $(p, T)$  phase diagram of KDP.

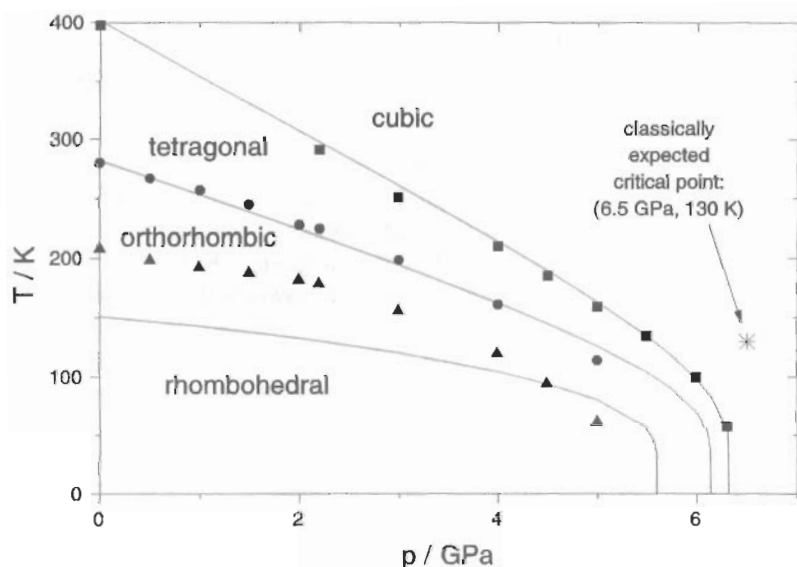
The case of  $\text{BaTiO}_3$  is more complex, for several reasons. Firstly, there is a sequence of phase transitions ( $P \ m3m - P \ 4mm - B \ mm2 - R \ 3m$ ). In addition, the mechanism of the phase transition appears to be a mixture of displacive behaviour by the network of perovskite octahedra and order-disorder behaviour by the Ti within the octahedra [11]. The tetragonal—orthorhombic—rhombohedral transitions are first order (as is the cubic—tetragonal transition at low pressures). A Landau potential with a three component order parameter, quantum saturation, and coupling to the applied pressure [12] accurately describes the cubic—tetragonal—orthorhombic phase transitions in  $\text{BaTiO}_3$ , measured using dielectric constant measurements [13]. The phase diagram is shown in Fig. 4. The description of the orthorhombic—rhombohedral transition is less good; this may be because of the order-disorder aspect of these transitions, which is not as well described by a Landaulike model. More detailed structural analysis to examine this question is planned.



**FIGURE 3** The  $(p, T)$  phase diagram of  $\text{KH}_2\text{PO}_4$ , combining data from Samara [9] and Nelmes et al. [10]. Above the broken line, the paraelectric phase is stabilised by a classical combination of temperature and pressure. In the region between the broken and solid line, the paraelectric phase is stabilised by quantum mechanical effects, leading to a quantum paraelectric.

### Prospects

The quantum mechanical saturation temperature  $\theta_S$  is a property of phase transitions, which appears not to be affected by secondary variables in the way that the transition temperature is. As such, it has the potential to be a useful probe of the processes driving phase transitions.



**FIGURE 4** Pressure vs. temperature phase diagram for  $\text{BaTiO}_3$ , with the experimental data of Ishidate et al. [13] fitted to a quantum mechanical Landau potential by Hayward and Salje [12].

## References

1. G. A. Samara, The effects of deuteration on the static ferroelectric properties of  $\text{KH}_2\text{PO}_4$  (KDP). *Ferroelectrics* **5**, 25–37 (1973).
2. S. A. Hayward, M. C. Gallardo, and E. K. H. Salje, Ferroelectric phase transition in DKDP: A macroscopic order-disorder model. *Ferroelectrics* **255**, 123–137 (2001).
3. T. J. Holland and R. Powell, Thermodynamics of order-disorder in minerals. I. Symmetric formalism applied to minerals of fixed composition. *Am Mineral* **81**, 1413–1424 (1996).
4. R. J. Harrison and E. K. H. Salje, X-ray diffraction study of the displacive phase transition in anorthoclase, grain-size effects and surface relaxations. *Phys. Chem. Minerals* **21**, 325–329 (1994).
5. J. M. Pérez-Mato and E. K. H. Salje, Quantum fluctuations of order parameters in structural phase transitions and the pressure dependence of transition temperatures. *J. Phys. Condens. Matter* **12**, L29–L34 (2000).
6. P. J. Heaney, Phase transitions induced by solid solution. *Rev. Mineral.* **39**, 135–174 (2000).
7. S. A. Hayward and E. K. H. Salje, Low-temperature phase diagrams: non-linearities due to quantum mechanical saturation of order parameters. *J. Phys. Condens. Matter* **10**, 1421–1430 (1998).
8. T. Schneider, H. Beck, and E. Stoll, Quantum effects in an n-component vector model for structural phase transitions. *Phys. Rev. B* **13**, 1123–1130 (1976).
9. G. A. Samara, Vanishing of the ferroelectric and antiferroelectric states in  $\text{KH}_2\text{PO}_4$ -type crystals at high pressure. *Phys. Rev. Lett.* **27**, 103–106 (1971).
10. R. J. Nelmes, M. I. McMahon, R. O. Piltz, and N. G. Wright, High-pressure neutron-diffraction studies of  $\text{KH}_2\text{PO}_4$  type phase transitions as  $T_C$  tends to 0 K. *Ferroelectrics* **124**, 355–360 (1991).
11. B. Zalar, V. V. Laguta, and R. Blinc, NMR evidence for the coexistence of order-disorder and displacive components in barium titanate. *Phys. Rev. Lett.* **90**, 037601 (2003).
12. S. A. Hayward and E. K. H. Salje, The pressure-temperature phase diagram of  $\text{BaTiO}_3$ : a macroscopic description of the low-temperature behaviour. *J. Phys. Condens. Matter* **14**, L599–L604 (2002).
13. T. Ishidate, S. Abe, H. Takahashi, and N. Môri, Phase diagram of  $\text{BaTiO}_3$ . *Phys. Rev. Lett.* **78**, 2397 (1997).