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## Evolution of the ferroelectric transition character of partially deuterated triglycine selenate

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**Abstract.** Automatically recorded hysteresis loops and dielectric constant data on pure and partially deuterated triglycine selenate and sulphate are used to characterize the transition evolution from quasi-tricritical to clearly first order character. A quantitative assessment of the transition's displacive degree is made through the first anharmonic contribution to the effective field ( $g$ ), obtained from hysteresis loop data. This characterization is complemented with the assessment by means of a generalized Rhodes–Wohlfarth parameter  $R = (Nk_B C / 4\pi P_{S0}^2)^{1/2}$  involving the Curie constant  $C$  and the saturation spontaneous polarization.  $P_{S0}$  as done previously by other authors.

### 1. Introduction

First principles local density approximation calculations [1] on ferroelectric perovskites have shown that cubic/tetragonal phase transitions in some of these compounds, at first thought to be of the displacive kind, can be well described as order/disorder type transitions. On the other hand, generalized Rhodes–Wohlfarth empirical parameters [2–4], analogous to those used to characterize magnetic phase transitions, have been proposed to assess quantitatively the displacive versus order/disorder degree of ferroelectric transitions.

In this work we focus our attention on transitions in hydrogenated and deuterated crystals of triglycine selenate  $(\text{TGSe})_{1-x}(\text{DTGSe})_x$ , and triglycine sulphate  $(\text{TGS})_{1-x}(\text{DTGS})_x$ , which are paradigmatic examples of order/disorder transitions but are not free from typical features of displacive systems such as the discontinuous, first order transition observed in DTGSe. We will see that in these ferroelectrics (whose structure is so complicated as to preclude *ab initio* calculations to substantiate the mixed displacive–order/disorder character) it is still possible to quantitatively characterize the evolution of the displacive component involved in the phase transition. The order/disorder features of a transition may be ascertained through measurements of the transition entropy and the specific heat jump at  $T_C$ . The displacive characteristics are usually (if it is at all feasible) seen by measuring underdamped soft modes in the vicinity of the transition by means of infrared, Raman or neutron scattering spectroscopies. Recently Dalal *et al* [5] have pointed out that diffraction work and NMR data provide convincing evidence that order/disorder and displacive features coexist in H bonded ferroelectric transitions. Characteristics of mixed order/disorder–displacive phase transitions can be analysed within the framework of a generalized effective field approach in which the effective field is given by

$$E_{eff} = E + \beta P_d + \gamma P_d^3 + \delta P_d^5 \dots$$

The basic differences between a purely order/disorder and a purely displacive transition, if such extreme cases are possible [4] at all among ferroelectric transitions, can be visualized in the following way. In an *order/disorder transition* an ion (atom) or a group of ions (atoms) in the unit cell may occupy either one of two 'off centre' (shifted) positions between neighbouring ions (atoms). These two positions correspond to two potential well minima separated by a relatively large energy barrier at the mid-point between them. In the paraelectric phase the two potential minima are equivalent, and they are equally populated. In the ferroelectric phase the cooperative (dipolar) interaction between cells makes the two wells become asymmetric and a spontaneous polarization sets in. Even at the order/disorder transition, if the two potential minima are deep enough and their separation is well kept, harmonic oscillations around the equilibrium position may be well defined and the normal modes may remain 'hard'. On the other hand, in a *displacive transition*, corresponding to the case of a shallow well separated by a weak potential barrier, the separation between the minima (at which the potential may require additional anharmonic terms to be well specified) would evolve from the low temperature ferroelectric phase towards the transition point and beyond, into the paraelectric phase. At these higher temperatures we would finally have one single effective minimum and the anharmonic oscillations around equilibrium could result in 'soft' modes.

Depending on the relative sign of higher order terms in the local potential, the dipole moment in the paraelectric phase ( $T \geq T_C$ ) could be either larger or slightly smaller than in the ferroelectric phase ( $T \cong 0$  K).

Triglycine selenate, belonging to the triglycine sulphate family, is an interesting uniaxial ferroelectric whose transition is very close to a tricritical point [6–8]. Increasing deuteration changes the transition's features giving rise to a clearly *discontinuous* transition with a thermal hysteresis  $\Delta T \cong 0.8$  °C for  $x = 0.96$ , almost full deuteration [9]. The availability of accurate dielectric and thermal data near the Curie temperature for both TGSe and TGS is important to assess quantitatively the evolution with deuteration of the degree of displacive character of the phase transition.

## 2. Experiment

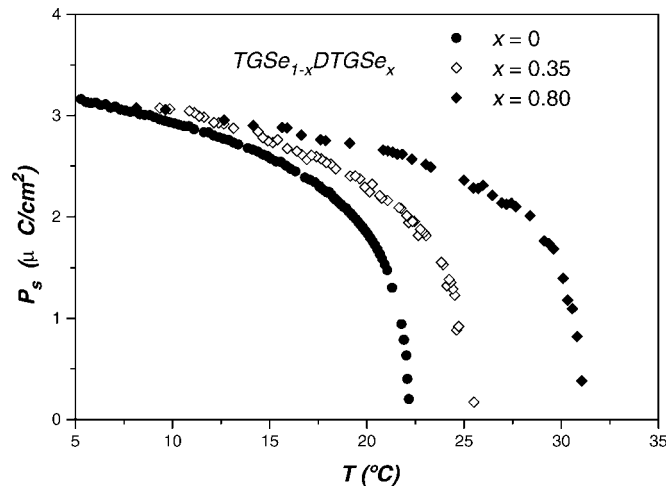
The samples of TGSe and TGS were prepared at the Institute of Physics, Adam Mickiewicz University, Poznan (Poland). They were cut from single crystals grown from aqueous solution and their shape was almost parallelepipedic. The thickness of these samples was between 0.6 and 1.0 mm and their areas went from 3 to 25 mm<sup>2</sup>.

Hysteresis loops were measured at a frequency of 50 Hz with a DDP bridge and they were observed with a Nicolet NIC-310 digital oscilloscope. The temperature was carefully controlled by means of an Unipan 680 controller that allowed very slow heating/cooling ramps keeping an accuracy of 0.01 K. The actual temperature inside the sample holder was measured with a type T thermocouple connected to a Keithley 196 voltmeter. The sample holder was well isolated and refrigerated by liquid nitrogen. The whole measuring process was fully automated which resulted in a real improvement of the data acquisition. In fact, 4000 points were recorded for each loop at temperature intervals of 0.25 K and even lower (0.1 K) as the transition temperature was approached. After data recording, an iterative computer program was used to analyse the loops and to obtain the spontaneous polarization  $P_S$  at each temperature.

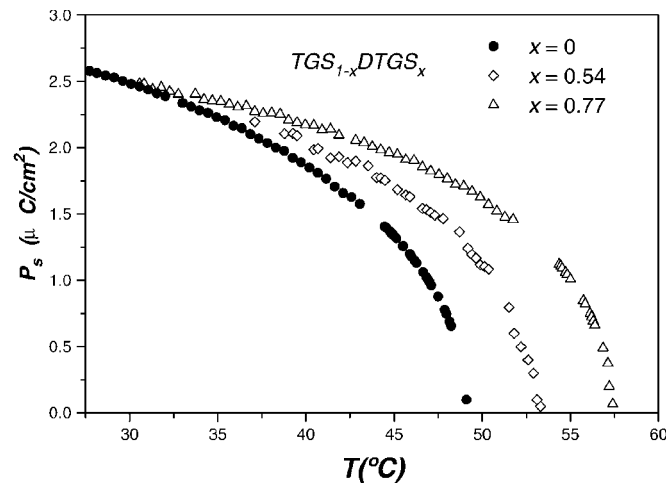
Dielectric constant measurements were performed with an HP 428A precision LCR meter at a low voltage of 1 V and a frequency of 1 kHz. Also these measurements were automatically programmed and recorded.

### 3. Results and discussion

Figure 1 gives the spontaneous polarization  $P_S$  against the temperature  $T$  for (a)  $(\text{TGSe})_{1-x}(\text{DTGSe})_x$ ,  $x = 0; 0.35; 0.80$ ; and (b)  $(\text{TGS})_{1-x}(\text{DTGS})_x$ ,  $x = 0; 0.54; 0.77$ . It can be seen that the decrease of spontaneous polarization approaching the transition temperature is more pronounced for TGSe than for TGS, as corresponds to quasi-critical behaviour, and that for DTGSe the data appear to suggest a small discontinuity at the transition.



(a)



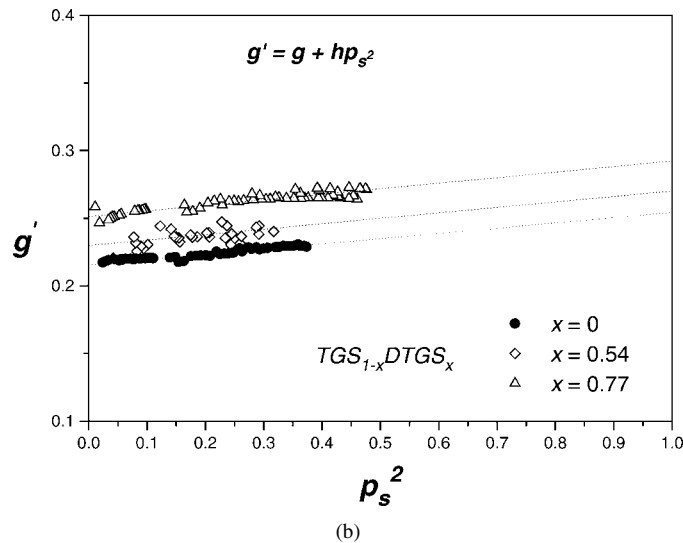
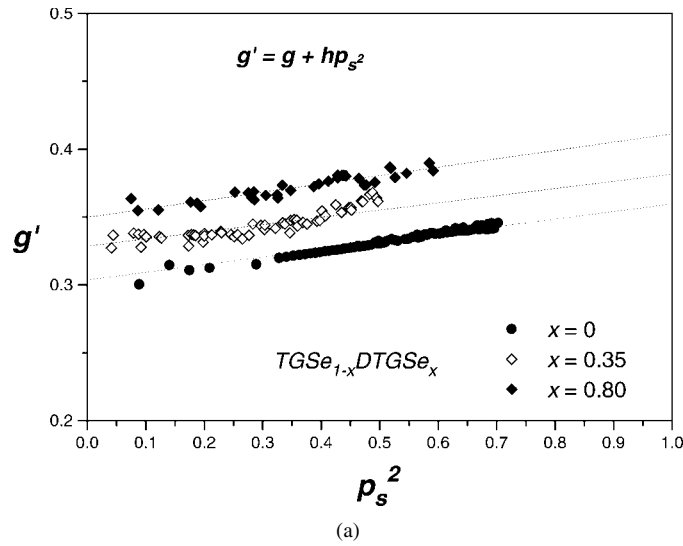
(b)

**Figure 1.** Spontaneous polarization  $P_{S0}$  against temperature  $T$  for different deuteration percentage in (a) triglycine selenate, and (b) triglycine sulphate.

Assuming an effective field of the form [10]

$$E_{eff} = E + \beta P_d [1 + g(P_d/N\mu)^2 + h(P_d/N\mu)^4 \dots] \quad (1)$$

where  $E$  is the external applied field,  $P_d$  is the dipolar polarization,  $N$  the number of dipoles per unit volume  $g, h$  a dimensionless coefficient and  $\mu$  the elementary dipolar moment. The dipoles



**Figure 2.** Linear plot of  $g'$  against normalized spontaneous polarization  $p_s^2$  for each deuteration percentage in (a) triglycine selenate, and (b) triglycine sulphate.

could be either rigid [ $\mu(T) = \mu(0) = \mu(T_C) = \text{constant}$ ] or deformable. In this later case there are two possibilities:  $\mu(T)/\mu(0) < 1$ , and  $\mu(T)/\mu(0) > 1$ , depending on the signs of higher order terms in the local potential.

From the equation of state

$$\frac{P_d}{N\mu} = \tanh\left(\frac{E_{eff}\mu}{k_B T}\right) \quad (2)$$

in terms of reduced variables  $e \equiv E/\beta N\mu$ ,  $p \equiv P_d/N\mu$ , we obtain

$$e = \frac{T}{T_C} \tanh^{-1} p - p(1 + gp^2 + hp^4 \dots) \quad (3)$$

**Table 1.** Dielectric measurements and resulting parameters.

	$x$	$T_C$ (K)	$\Delta T$ (K)	$P_{S0}$ ( $\mu C \text{ cm}^{-2}$ )	$g$	$C$ (K)	$R$
$(TGS\text{e})_{1-x}(\text{DTGS}\text{e})_x$	0	295.16	0.1	4.5	0.30	4166	0.87
	0.35	297.79	0.2	4.3	0.33	4000	0.89
	0.80	303.3	0.5	4	0.35	3703	0.92
$(TGS)_{1-x}(\text{DTGS})_x$	0	322.18	—	4.2	0.21	3225	0.82
	0.54	326.15	—	3.9	0.23	2941	0.84
	0.77	330.4	—	3.6	0.25	2702	0.87

and with  $p = p_s$  (the reduced spontaneous polarization) for  $e = 0$ , we have

$$g'(p_s^2) \equiv g + hp^2s \simeq \frac{[(T/T_C)(\tanh^{-1} p_s)/p_s]}{p_s^2} - 1. \quad (4)$$

We note that each hysteresis loop provides a spontaneous polarization  $P_S(T)$  which is normalized,  $p_s(T) = P_S(T)/P_{S0}$ , with  $P_{S0} \equiv N\mu$ , to be introduced in equation (4).

Figure 2 gives  $g'$  against  $p_s^2$  for (a)  $(\text{TGS}\text{e})_{1-x}(\text{DTGS}\text{e})_x$  and (b)  $(\text{TGS})_{1-x}(\text{DTGS})_x$  for the different molar fractions. As the plots can be linearly fitted we can determine  $g$  as the value at which each fitting line crosses the  $g'$  axis. The coefficient  $g$ , representing the strength of the quadrupolar interaction [11–13], is a good indicator for the type of transition of the ferroelectric crystal. In fact,  $g < 1/3$  for a second order transition,  $g > 1/3$  for a first order transition and  $g = 1/3$  for a tricritical point.

We had checked in an earlier work [14] that increasing deuteration in TGS determines an evolution of the transition to a tricritical point but staying still far from it. In a similar way for TGSe, the first order character of the ferroelectric transition becomes more evident [9] as the percentage of deuteration grows. As the transition becomes more first order the  $g$  value grows [13], reflecting likely changes in the local potential.

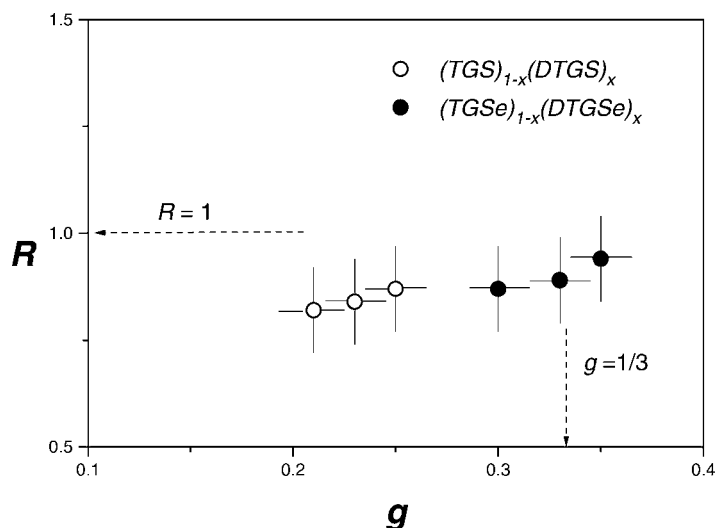
An entirely different parameter,  $R \equiv \mu_c/\mu_0$ , analogous to the Rhodes–Wohlfarth parameter for magnetic systems as previously mentioned, has been proposed [3,4] to characterize the ferroelectric transition type. Here  $\mu_c$  is defined as the individual dipolar moment in the paraelectric phase, obtained from the Curie–Weiss constant,  $C = \varepsilon(T - T_C)$ , with  $\varepsilon$  the low field and low frequency dielectric constant; and  $\mu_0$  is taken as the saturation individual dipolar moment in the ferroelectric phase ( $T = 0$  K), given by  $P_{S0}/N$ . So we can write

$$R \equiv (Nk_B C / 4\pi P_{S0}^2)^{1/2}.$$

It is evident that in an order/disorder ferroelectric, with rigid dipoles approximately equal in the paraelectric phase and at saturation ( $T \simeq 0$  K) the value of  $R$  must be near one. As the displacive character of the transition becomes more and more pronounced one expects that going through  $T_C$  involves not only disordering the preferentially aligned dipoles but also releasing their strain (related to the spontaneous field and to the anharmonic potential terms). It may be then expected that the generalized Rhodes–Wohlfarth parameter becomes larger than one.

Table 1 shows the values obtained from hysteresis loops and dielectric constant measurements for the six different samples.

Figure 3 gives  $R$  as a function of  $g$  for pure and deuterated TGS, and pure and deuterated TGSe. It can be seen that there is a linear correlation between both parameters. In the plot we have noted  $g = 1/3$  (that indicates the crossover between continuous and discontinuous transitions), and  $R = 1$  (which is the borderline between the dipole behaviour upon crossing



**Figure 3.** Plot of Rhodes–Wohlfarth parameter  $R$  against  $g$  for triglycine selenate and triglycine sulphate with different deuteration percentages. Each point can be identified from the values recorded in table 1.

the transition). The above data show clearly that  $R$  grows when  $g$  grows and that  $R > 1$  favours the displacive character of the transition which becomes more likely to be first order ( $g > 1/3$ ).

We may then conclude that the parameter  $g$ , which can be easily obtained from hysteresis loop data for most ferroelectric crystals, gives a good characterization of the transition in uniaxial, basically order/disorder ferroelectrics ( $0 \leq g \leq 1/3$ ) as well as in typically displacive ferroelectrics ( $g \approx 1$ ) like most pseudocubic ferroelectric perovskites. Cases like  $\text{LiTaO}_3$  which can be considered a highly distorted perovskite are good examples of the coexistence of pronounced order/disorder and displacive features. The case of  $\text{Sn}_2\text{P}_2\text{S}_6$ , with a second order transition at  $T \approx 337$  K is another example of a transition which can be said to be at the order/disorder—displacive crossover [15].

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