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INFLUENCE OF LATTICE DEFECTS ON THE CRITICAL BEHAVIOUR OF TGS SINGLE CRYSTALS

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The influence of radiation defects and foreign ions on the critical behaviour of TGS is studied by the dielectric method. The temperature width of the critical region (where the critical point indices $\gamma, \gamma' \neq 1$) is found to increase with defect concentration; however, beyond this region the critical indices are found to be unaffected by lattice defects. Rejuvenation causes the temperature width of the critical region to decrease.

1. *Introduction*

One of the most important problems of molecular physics resides in the mechanism of phase transitions. In the case of ferroelectric crystals, the role of long range order dipole-dipole interaction in the occurrence of the paraelectric-ferroelectric phase transition has to be elucidated. This transition is accompanied by a critical behaviour of the physical quantities. Critical phenomena are usually described in terms of a set of indices, referred to as the critical point exponents [1, 2]. A critical point exponent λ is defined as:

$$\lambda = \lim_{\varepsilon \to 0} \frac{\ln f|\varepsilon|}{\ln |\varepsilon|}, \tag{1}$$

where $\varepsilon = (T-T_c)/T_c$, and T_c denotes the critical temperature. Two main reasons can be invoked for the common use of critical point exponents, which obviously convey considerably less information than the complete function $f|\varepsilon|$. The exponents can be established by experiment, whereas this is not the case for the complete functional form $f|\varepsilon|$ of a given physical quantity. Moreover, the relations between exponents describing the critical behaviour of various physical quantities are known (general, proved exponent inequalities, and unproved scaling hypotheses, which predict the inequalities to be satisfied as equalities).

The aim of our work was to clarify the role of lattice defects in the paraelectric-ferroelectric phase transition. For various reasons, TGS crystals were used. First, in TGS the

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paraelectric-ferroelectric phase transition is of second order, and the dielectric critical behaviour for pure TGS crystals is available from the work of various authors [3–6]; however, the temperature width of the critical region reported differs. Second, the nature of defects in TGS introduced by irradiation or doping has been established by other methods [7–13]. The influence of radiation defects as well as foreign ions on the critical behaviour of the static dielectric properties of TGS has been studied extensively.

We assume the measured dielectric permittivity ε to be of the form:

$$\frac{1}{\varepsilon}=\frac{1}{\varepsilon_0}+A^{\pm}\left(\frac{|T-T_c|}{T_c}\right)^{-(\gamma,\gamma')}, \tag{2}$$

where γ and γ' denote respectively the critical point exponents above and below the critical temperature T_c (defined as the temperature of the intersection point of extrapolated Curie–Weiss law straight lines), and ε_0 denotes the effective dielectric permittivity related to series capacitance of the surface layers [4]. The critical point exponents, as well as the temperature width of the critical region i.e. the region where deviation from the Curie–Weiss law occurs, are determined for pure and defected crystals.

2. *Experimental results*

TGS single crystals were grown from aqueous solution in the paraelectric phase by isothermal evaporation at the stoichiometric pH value. To the solutions from which Cu^{2+}- and Cr^{3+}-ion doped crystals were grown, 3 weight percent of $CuSO_4$ and 1 weight percent of $Cr_2(SO_4)_3$ were added, respectively. Radiation defects were introduced by γ-Co-60 irradiation at a dose rate of 200 Gy/h. Samples in the form of discs 0.5 cm in diameter and about 0.1 cm thick with gold evaporated electrodes were maintained in a sample holder. Special care was taken to avoid mechanical stress on the sample surfaces from the electric contacts. The sample holder, introduced into a glass vessel, was termostatized, and the temperature variations were about 0.005 K/min. The capacity of the samples was measured at a frequency of 10 kHz by means of a 4270 A hp-automatic capacitance bridge.

Fig. 1 shows the $\log\left|\frac{1}{\varepsilon}-\frac{1}{\varepsilon_0}\right|=f\left(\log\frac{|T-T_c|}{T_c}\right)$ dependence for a typical non-selected pure TGS sample and samples γ-irradiated with doses of 2.5 kGy, 12 kGy, and 25 kGy, respectively. The critical exponents, calculated by the mean squares method for about 300 measuring points both in the para- and ferroelectric phases, are shown. It can be seen that the temperature width of the critical region for a typical pure TGS sample is of about $|T-T_c|/T_c \simeq 5\cdot 10^{-4}$. This width is found to increase with defects concentration. Fig. 2 shows the dose dependence of the critical region width ΔT_{crit} measured both in the para- and ferroelectric phase.

The temperature width of the critical region is found to increase also due to defects introduced in the form of foreign ions. ΔT_{crit} for TGS : Cu^{2+} crystals measured just after termination of growth is 0.65 K, whereas for TGS : Cr^{3+} crystals it equals 3.45 K. Moreover, the temperature width of the critical region is found to decrease after rejuvena-

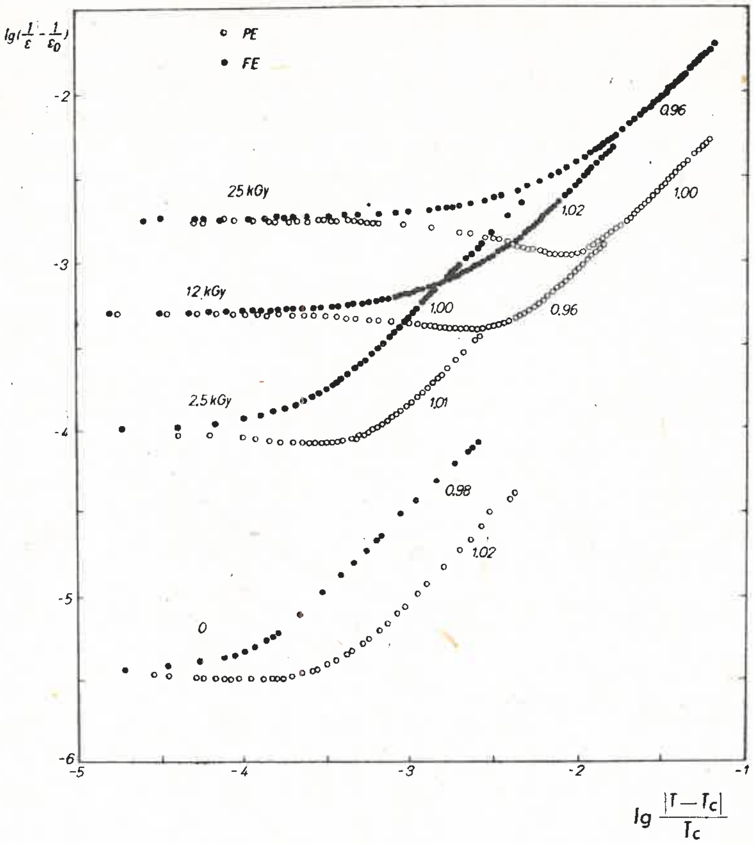

Fig. 1. Log-log plot of the inverse dielectric permittivity versus the fractional temperature distance from the Curie point for TGS nonirradiated and γ-irradiated with various doses

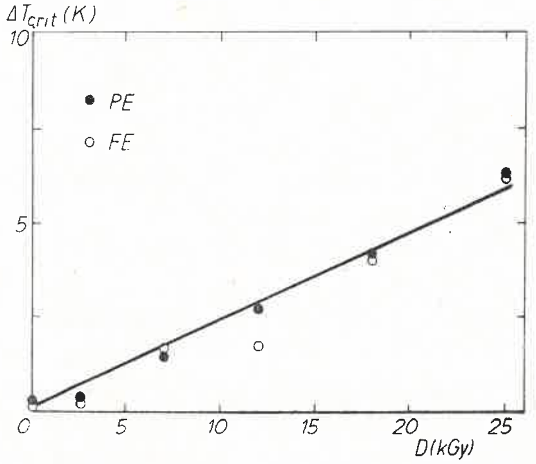

Fig. 2. ΔT_{crit} versus the dose of irradiation (● PE — in the paraelectric and ○ FE — ferroelectric phase)

tion. Fig. 3 shows $\log\left|\frac{1}{\varepsilon}-\frac{1}{\varepsilon_0}\right| = f\left(\log\frac{|T-T_c|}{T_c}\right)$ for TGS : Cr^{3+} doped sample just after termination of growth and rejuvenated 100 hs at a temperature of 70°C. It can be seen (Figs. 1 and 3) that the values of the critical exponents are, in general, unaffected by lattice defects.

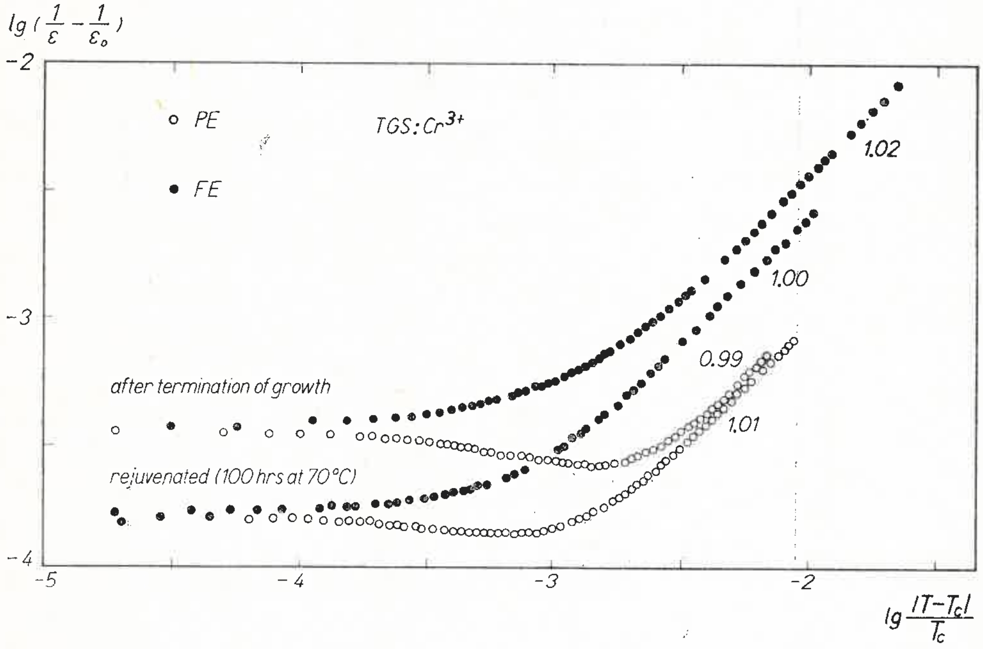

Fig. 3. Log-log plot of the inverse dielectric permittivity versus the fractional temperature distance from the Curie point for TGS: Cr^{3+} (grown from solution doped with 1 weigth percent of $Cr_2(SO_3)_3$) just after termination of growth and after rejuvenation (100 hrs at 70°C)

3. *Conclusions*

There are several theoretical models of the phase transitions and each of them predicts a given set of critical exponents, irrespective of the location of the critical point. The Mean Field Theory (MFT) originating from the Weiss phenomenological theory of ferromagnetism gives the same values for each of the exponents as other so-called classical theories (e.g. Landau theory [1]). In particular, the values of the critical-point exponents γ and γ' predicted by MFT are equal to 1.

As far as static properties are concerned, a deviation from the classical behaviour of a uniaxial ferroelectric with strong dipolar interaction is expected to occur only in an extremely narrow temperature region near the second order phase transition [14]. This is the case of TGS crystals; however, it seems that the width of the critical region cannot be calculated explicitly. Attempts to assess the critical region width are limited by the large uncertainty in the determination of the energy of the short-range correlations of the polarization fluctuations [15, 16]. Recently, Nattermann [17] has estimated the width of the critical region in TGS as equal to $|T-T_c|/T_c = 1.6 \cdot 10^{-2}$ and $1.8 \cdot 10^{-3}$.

It has been found by various authors [3–6, 16, 18, 19] that, sufficiently far from the critical temperature, the predictions of MFT are obeyed for TGS crystals both in the para- and ferroelectric phase; however, the temperature ranges of the critical region obtained are different. For selected pure TGS samples the critical region is extremely narrow [5], $|T-T_c|/T_c \lesssim 3 \cdot 10^{-5}$, and its width depends on the annealing conditions [6]. Some authors claim [14] that the width of the critical region, (defined as the temperature region in which a significant deviation from the MFT predictions takes place) depends on the quality of the crystal. Our measurements confirm these statements; however, in Fig. 1 an example for a typical pure TGS crystal, grown in our laboratory is presented. The temperature width of the critical region defined above was found to be strongly dependent on imperfections. For γ-Co-60 radiation induced defects, e.g. CH_2COO^- and NH_3CHCOO^- free radicals [7–9] and point defects created by internal irradiation with Compton electrons [13], a linear increase in the temperature width of the critical region is observed. It is accompanied by a marked shift in Curie point towards lower temperatures reported earlier [20, 21]. In the case of doped TGS crystals, where generally Glycine II and Glycine III groups form complexes with foreign ions [10–12], the influence of defects on the critical temperature T_c is found to be small (not greater than 1 K); however, the temperature width of the critical region increases. The rejuvenation process causes the above mentioned width to decrease.

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