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Effect of Defects and Impurities upon the Phase Transition in TGS Crystals

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The influence of γ-irradiation upon the thermal and elastic properties of high quality TGS crystals was studied. It is shown that small doses of irradiation (up to 0.5 MR) change the critical behaviour of the specific heat and elastic stiffness. The effect is described within the theory proposed by Levanjuk and others. The density of point defects arising after irradiation was estimated using the theory and found to be $N=3 \cdot 10^{19}$ cm^{-3} for the dose $D=0.1$ MR and $N=1 \cdot 10^{20}$ cm^{-3} for $D=0.3$ MR. The larger doses of irradiation result in the progressive smearing of the phase transition anomalies and their suppressing.

The problem of defects and impurities influence upon the phase transition in ferroelectrics received significant attention lately. The most important goal of such study is to find out what properties of the crystals are really intrinsic and which ones connected with an inevitable defectness. For the quantitative analysis of the problem it seems reasonable to find first the model of "ideal" crystal; the the dosed out implementation of the defects in such a model may present a chance to follow a change of the crystal critical behaviour.

The most accessible object for such a study seems to be TGS crystals and the appropriate way to change their quality is γ-irradiation presumably producing point defects in the crystal lattice.

The recent theoretical study of the problem[1] shown that defects can produce the drastic change of the critical behaviour. The question is what kind of TGS crystals one may count as perfect one. As to our data high quality TGS crystals grown above T_c are the most perfect and can be taken as a model of the defectiveless crystals.

The temperature dependences of the specific heat C_E measured by a vacuum adiabatic calorimeter at the short-circuit crystal mentioned above and ultrasound longitudinal waves velocity along Z-axis V_z ($f=10$ MHz) are presented in Figs. 1 and 2. It is seen that the anomalous change of C_E and V_z in paraelectric phase occur within the temperature interval of about 0.02–0.03 K and follow Landau theory with this accuracy. The surplace specific heat and ultra-

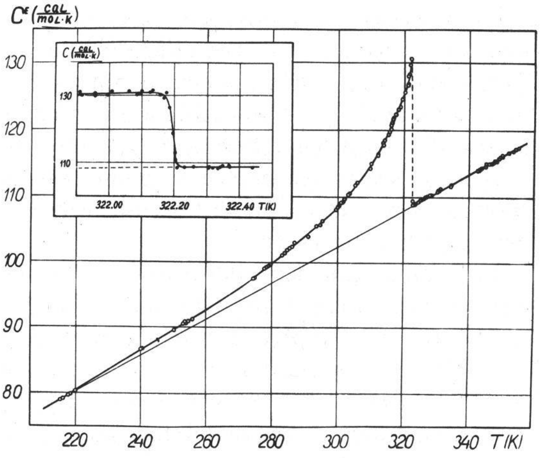

Fig. 1. Temperature dependence of the specific heat for A-type TGS crystals.
Insertion: the very vicinity of T_c.

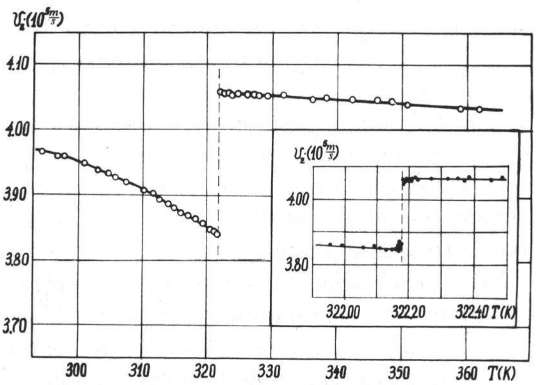

Fig. 2. Temperature dependence of ultrasonic longitudinal waves along Z-axis ($f=10$ MHz) for A-type TGS crystals.
Insertion: the very vicinity of T_c.

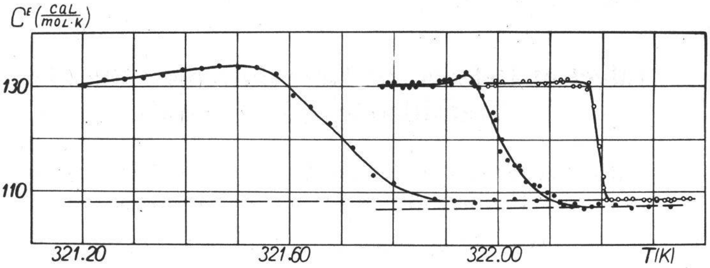

Fig. 3. Temperature dependence of the specific heat for A-type TGS crystals for different doses of γ-irradiation: ○– $D=0$ MR; ●– $D=0.1$ MR; ◐– $D=0.3$ MR.

sonic velocity were not observed above T_c with 0.1% accuracy. Any anomaly of ultrasonic longitudinal waves velocity along polar axis was not registered at T_c as well.

We have a good reason to believe that TGS crystals grown above T_c (A-type TGS crystals) are more perfect than those grown below T_c (B-type TGS crystals);[2] so the difference for the TGS specific heat behaviour near T_c reported by number of authors[3-6] probably was caused by crystal imperfections differing from sample to sample. It seems reasonable to count A-type crystals as a model representing intrinsic properties of the substance.

The temperature dependence of $C_{E=0}$ for the original and small doses γ-irradiated A-type crystal ($D=0.1$; 0.3 MR) is presented in Fig. 3. It is seen that γ-irradiation shifts the transition point ($\mathrm{d}T_c/\mathrm{d}D=-1.75$ K/MR). In addition the surplace specific heat above and slight increase of C_E below shifted Curie point appear. It should be stressed at once that such an evolution of the $C_E(T)$ dependence can not be interpreted in the framework of an inner biasing field conception. It is interesting to point as well that small doses irradiated A-type crystals possess a $C_E(T)$ dependence which is similar to one for the original B-type crystals.

The resembling results were obtained for $V_z(T)$ dependences of γ-irradiated A-type crystals which relate to $C_E(T)$ ones within Pippard-Janovec equation for both para- and ferroelectric phases.

The obvious reason for the critical anomalies variations after irradiation is the point defects of the crystal lattice. So let us try to analyse the experimental results within the phenomenological theory developed in ref. 1. We shall count that the point defects in the uniaxial ferroelectric under consideration (P_z is an order parameter) can be determined by the polarisation value at the spherical nucleus with a radius which is to be equal "d". In a continuum approximation the free energy function of the crystal containing one defect can be introduced as

$$F=2\pi\delta d(P_{z0}-P_{z\infty})^2 \times\left\{1+\frac{\pi^{\frac{1}{2}}d}{\delta^{\frac{1}{2}}}\left[1-\frac{\delta}{8\pi r_c^2}\ln\frac{A}{16\pi}\right]\right\} \qquad (1)$$

with all notations accepted in ref. 1. For noninteracting defects (small doses of irradiation used in experiments) their contribution into free energy will be additive. The specific heat defects-stipulated part can be obtained by usual method:

$$\Delta C=\frac{Nd^3P_{z0}^2A_0^2}{4T_c}\left(1+\sqrt{\frac{\pi}{A_0}}\right)\tau^{-1} \qquad (2)$$

where $\tau=(T-T_c)/T_c$, $A\tau^{-1}$—the coefficient at P_z^2 in the free energy expansion. The range of applicability of eq. (2) coincides with Levanjuk-Ginzburg criterion; note that obtained τ^{-1}-dependence occurs to be more strong than fluctuation one where $\Delta C\sim\ln\tau$.[7]

To compare (2) with the experiment we ploted the anomalous part of C^E at $T>T_c$ for irradiated crystals (Fig. 4) as a function of τ^{-1}. As it is seen from Fig. 4 the curves have a linear parts which tilts increase when the defect concentration goes up. No such a part was observed for nonirradiated crystal. For the numerical estimation one can take reasonable values for $d\sim5\cdot10^{-8}$ cm and $P_{z0}\sim3\ \mu C\cdot\mathrm{cm}^{-2}$ and obtain for the defects concentration

$$N=3\cdot10^{19}\ \mathrm{cm}^{-3}\ \text{for}\ D=0.1\ \mathrm{MR},$$
$$N=1\cdot10^{20}\ \mathrm{cm}^{-3}\ \text{for}\ D=0.3\ \mathrm{MR}.$$

The rise of the defects concentration with dose as well as the appropriate order of N values points that experimental data are adequate to the model of ref. 1.

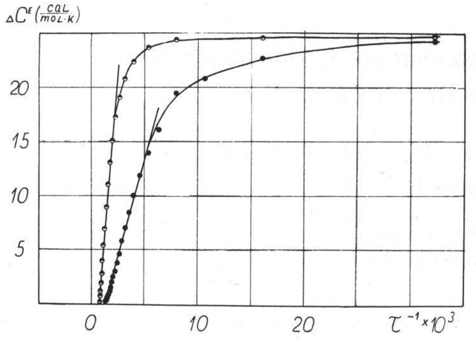

Fig. 4. Specific heat of *A*-type TGS crystals as function of τ^{-1}.

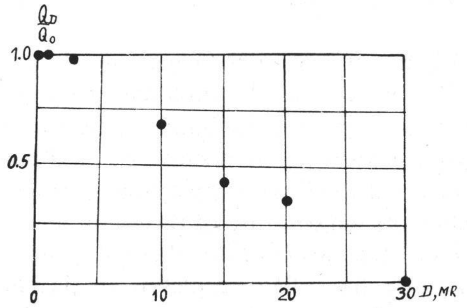

Fig. 5. Relative surplace energy of the phase transition for TGS crystals as a function of irradiation dosage.

The larger doses of irradiation result in the increasing shift of the transition point to lower temperature, progressive smearing of the anomalies and their suppressing.[8] Doses $D>1$ MR cause an essentual destruction of the lattice manifesting itself in the reduction of the phase transition energy (Fig. 5).

Finally we hope that listed results throw some light on a real nature of TGS phase transition anomalies. Both implanted and original defects can really change a critical behaviour masking the intrinsic properties of crystals.

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