Heat capacity anomalies in γ-irradiated triglycin sulfate crystals

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For the first time the evolution of the heat-capacity anomaly has been studied in triglycin sulfate crystals irradiated with small doses of γ rays. From comparison of the results with a phenomenological theory taking into account the effect of noninteracting defects on the nature of anomalies in the phase-transition region, the concentration of defects produced in crystal by irradiation has been estimated.

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The main cause of anomalies of various physical parameters of a substance near a point of second-order phase transition T_c is assumed to be thermodynamic fluctuations of the order parameter, whose intensity increases sharply as $T \to T_c$. However, at present there is a view that temperature anomalies may be due to crystal-lattice defects which can be treated as "frozen fluctuations."[1] When lattice distortions caused by the defects correspond to the order parameter, the dimensions of the defect-disturbed region will increase as $T \to T_c$ as a result of the increasing radius of correlation of the order parameter.

It is highly interesting, therefore, to conduct a systematic experimental investigation of the influences exercised by defects on the thermodynamic characteristics of crystals near T_c. We have shown earlier[2] that in ferroelectric triglycin sulfate (TGS)

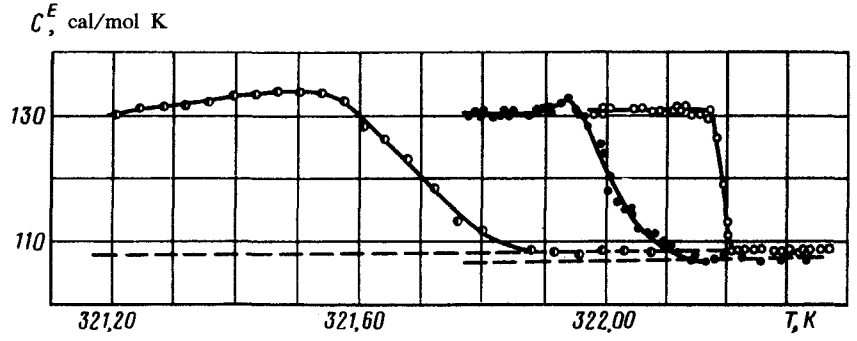

FIG. 1. Temperature dependence of the heat capacity of TGS crystals grown at $T > T_c$ for irradiation doses: ○—$D = 0$ mR, ●—$D = 0.1$ mR, ◐—$D = 0.3$ mR.

crystals grown in equilibrium conditions at $T > T_c$ there is a jump of the sound velocity at $T = T_c$, the width of the step being less that 0.03 K. We have thus obtained an object that can be considered "ideal" and has properties that fit the Landau theory with a high accuracy.

This paper presents the results of a study of the heat capacity of a TGS crystal grown at $T > T_c$ as a function of the γ irradiation dose.

Figure 1 shows the temperature dependence of the heat capacity of a short-circuited (electric field $E = 0$) TGS crystal, unirradiated and irradiated with doses $D = 0.1$ and 0.3 mR. It is evident that the anomaly of the heat capacity of the unirradiated crystal has the shape of a 0.02–0.03 K wide step, i.e., is close to data obtained from sound-speed measurements in Ref. 2.

As the result of γ irradiation, the phase-transition point is shifted towards lower temperatures ($dT_c/dD = 1.75$ K/mR); besides, excessive heat capacity appears above the displaced phase-transition point. The evolution of the dependence $C_E(T)$ with increasing D cannot be interpreted simply as a smearing of the phase transition, since the heat capacity at $T < T_c$ in the irradiated crystal is somewhat increased.

We note that the anomaly of the heat capacity in the irradiated crystal is analogous to the earlier data on the heat capacity of TGS crystals grown $T < T_c$. This suggests as the only possible cause of these anomalies the lattice defects produced in the crystal during irradiation, or during crystal growth in a polar phase.

Let us analyze this result in terms of the phenomenological theory presented in Ref. 1. We will assume that a point defect in a maximally anisotropic ferroelectric with one spontaneous polarization axis (order parameter P_z) can be defined by the polarization P_z on a spherical nucleus of radius d.

In continuum approximation the free energy of a single-defect system can be expressed as

$$F_1 = 2\pi\delta d (P_{z0} - P_{z\infty})^2 \left\{ 1 + \frac{\pi^{1/2} d}{\delta^{1/2}} \left[1 - \frac{\delta}{8\pi r_c^2} \ln \frac{A}{16\pi} \right] \right\}, \quad (1)$$

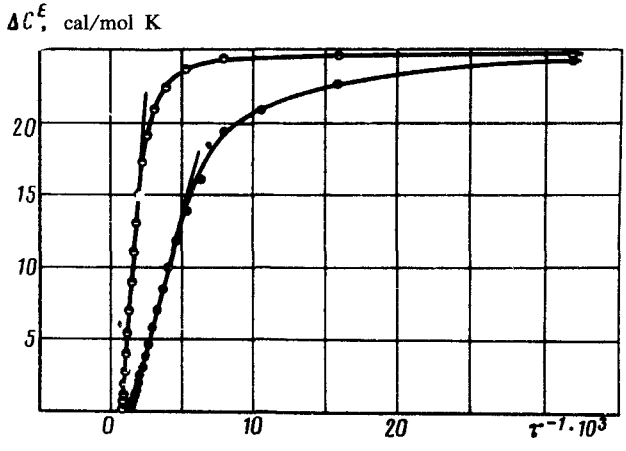

FIG. 2. Temperature dependence of the heat capacity of irradiated TGS crystals as a function of τ^{-1}: ●—$D = 0.1$ mR, ○—$D = 0.3$ mR.

where the notation is the same as Ref. 1, except for the symbol of the correlation parameter (in Ref. 1, $\delta \to D$).

Assuming the concentration of defects N sufficiently small for the approximation for noninteracting defects to be applicable (the condition of additivity of defect contributions to free energy), we obtain, after double temperature differentiation and averaging over the system of randomly distributed defects, the expression for the contribution of defects to the heat capacity for $T > T_c$

$$\Delta C \approx N \frac{d^3 P_{z0}^2 A_0^2}{4 T_c} \left(1 + \sqrt{\frac{\pi}{A_0}}\right) \tau^{-1} . \tag{2}$$

Here $\tau = (T - T_c)/T_c$, and $A_0 = A\tau^{-1}$ is the temperature-independent coefficient of the quadratic term in the expansion of the free energy in even powers of P_z. The region of applicability of this expression is determined by the Ginzburg-Levanyuk criterion and the condition of applicability of the approximation of noninteracting defects.

Note that the obtained temperature dependence $\Delta C \sim \tau^{-1}$ is stronger than the fluctuation dependence, where $\Delta C \sim \ln|\tau|$.[3]

Let us compare (2) with the experimental data. For this we plot the anomalous part of the heat capacity for $T > T_c$ as a function of τ^{-1} (Fig. 2). It can be seen that for the irradiated crystals there is a linear part in the temperature dependences $\Delta C(\tau^{-1})$ with a slope which increases with the concentration of defects. For the unirradiated crystal there is no such region. For numerical evaluation let us adopt approximate values $d \sim 5 \times 10^{-8}$ for the size of the defect nucleus and $P_{z0} \sim 3\mu C/\text{cm}^2$, the order parameter in the region of localization of the defect. Then, for the defect concentration we have

$N = 3 \times 10^{19}$ cm^{-3} for $D = 0.1$ mR,

$N = 1 \times 10^{20}$ cm^{-3} for $D = 0.3$ mR.

The growth in defect concentration with irradiation dose, as well as the order of magnitude of N, indicates that these experimental data are in good agreement with the model discussed in Ref. 1. The effects due to a displacement of the phase-transition point caused by a defect-induced change in the effective dimensions of the nucleus were disregarded in Ref. 1. The displacement of the transition point in this case is due to mechanical stresses and is proportional to the defect concentration N. At larger irradiation doses ($D > 1$ mR) there arise macroscopically damaged regions caused by radiolysis of the material with a rapid "smearing" of the phase transition and decrease of all its characteristic anomalies.

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