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Change in the Order of the Phase Transition in Triglycine Selenate Crystal

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The specific heat of a partly deuterated triglycine selenate (DTGSe) crystal under γ-irradiation was measured. It was shown that γ-irradiation defects changed the thermodynamic behavior of DTGSe crystal in a small dose region. The order of the phase transition changed from the first to the second at D=0.3 MR.

Key words: DTGSe, γ-irradiation, Phase transition, Tricritical point

I. Introduction

Triglycine selenate (TGSe) is a ferroelectrics having an isomorphous structure with triglycine sulfate and fluoroberyllate.[1] The Curie point of TGSe is about 22°C.[2] The ferroelectric phase transition in TGSe crystal is of the second order just like that in TGS. It is well known that the second order phase transition in TGSe crystal is very close to the tricritical point (TCP).[3] It is possible to change the order of the phase transition by hydrostatic pressure[4] or H →D substitution in this crystal.[5] At normal pressure the substitutional TCP occurs at a deuterium concentration of x =0.3 in (H_{1-X}, D_X)TGSe crystal.[5]

It was shown that γ-irradiation of TGSe crystal results in a change of the Landau free energy expansion coefficients in such a way that the second order phase transition "moves away" from the TCP along the phase transition line.[6] Therefore the possibility of changing the phase transition order can be realized in DTGSe crystal by the defect concentration induced by γ-irradiation. Thus we assumed that for DTGSe crystal, possessing a deuterium concentration of x=0.3 and a first order phase transition, it is possible to use small doses of γ-irradiation to change the order of the phase transition from the first to the second through the TCP. In this case the concentration of irradiation defects can be considered as an independent thermodynamic parameter like hydrostatic pressure or deuterium content.

II. Experiments

The DTGSe crystal was obtained from a saturated solution of component under decreasing temperature after three recrystallizations in 99.7% D_2O. The deuterium content was determined from the relation:

$$x = \frac{T_x^D - T_c^H}{T_c^D - T_c^H} \quad (1)$$

where T_c^H and T_c^D are equal to the transition temperatures for pure and completely deuterated compounds, re-spectively. In our case T_x^D = 30.0°C which corresponds to x =0.62. (H_{1-x}, D_x)TGSe(x=0.62) crystal (m=6.94 g) was studied with the successive dose accumulation at room temperature. The source of γ-irradiation was Co^{60} with an intensity of 330 R/s. The phase transition was studied by specific heat measurement. An adiabatic calorimeter was used for the specific heat and latent heat measurements.

The surplus energy of the phase transition was measured by determination of the anomalous part of the heat capacity as

$$\Delta Q = \int_0^\infty (C_p - C_{Lat})dT \quad (2)$$

where C_{Lat} is the base(lattice) part of the specific heat. The temperature dependence of surplus heat capacity can be used for the determination of Landau expansion coefficients for different doses of γ-irradiation. The nearness of the transition to the TCP can be described by the quantity $K=\beta^2/4\alpha\gamma T_c$.

III. Results and Discussion

The results of the experiments are presented in Figs 1 and 2. It is shown from Fig. 1 that non-irradiated DTGSe (x=0.62) crystal has a typical first order phase transition close to a TCP. It is clear that in a small dose region the order of the phase transition was changed from the first to the second. The latent heat of the phase transition was determined directly by means of quasistationary thermograms (time dependence of the crystal temperature under constant power input). For a non-irradiated crystal the latent heat of the phase transition was ΔQ_L=186 J/mol. Fig. 2 shows that there is no detected latent heat from the dose 0.3 MR. It is clear that the order of phase transition in DTGSe(x=0.62) crystal changed from the first to the second for the dose D=0.3 MR (the TCP occurred at D=0.3 MR). And there was no smearing of the phase transitions even for the second order ones.

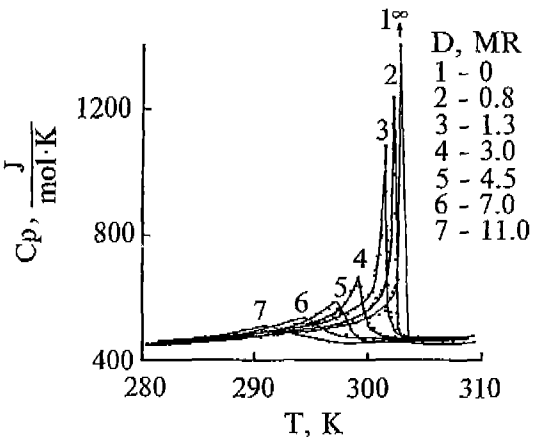

Fig. 1. Temperature dependence of specific heat for DTGSe (x=0.62) crystal for various doses of γ-irradiation.

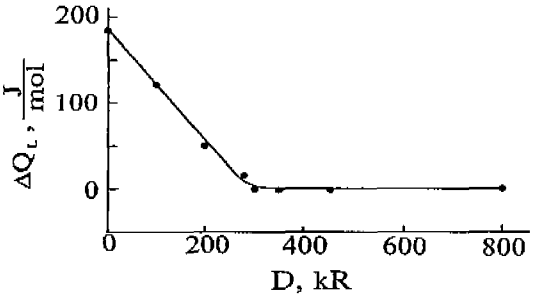

Fig. 2. Latent heat of the phase transition of DTGSe (x= 0.62) crystal for several doses of γ-irradiation.

Tricritical behavior can be described by the Landau phenomenological theory.[7] The theory is based on an expansion of the free energy ϕ by the order parameter η:

$$\Phi(p, T, \eta) = \Phi_0(p, T) + \frac{1}{2}\alpha(T - T_c)\eta^2 + \frac{1}{4}\beta\eta^4 + \frac{1}{6}\gamma\eta^6 \quad (3)$$

where T_c is transition temperature, and α, β, γ are the Landau free energy expansion coefficients. If the coefficient of sixth order term γ is positive, the character of the phase transition depends on the coefficient of the fourth term β. The phase transition at $T=T_c$ is of the first order for $\beta<0$ and of the second order for $\beta>0$, then the tricritical point (TCP) is realized at $\beta=0$, T=Tc. The coefficient β depends on some thermodynamic variables, e.g., pressure, concentration of solid solution, defects in the crystals.

The calorimetric and dielectric data allow us to determine α, β and γ coefficients by the following equation:

$$\left(\frac{\Delta C}{T}\right)^{-2} = \frac{4\beta^2}{\alpha^4} - \frac{16\gamma}{\alpha^3}\cdot(T - T_c) \quad (4)$$

The values of the Landau expansion coefficients for different doses of γ-irradiation are presented at Table 1. The coefficient of fourth term β is small and negative and becomes zero for D=0.3 MR and becomes positive (Fig. 3).

Table 1. Landau Expansion Coefficients for DTGSe (x=0.62) Crystal

D, MR	T_c, K	α, 10^{-3} (CGS)	β, 10^{-10} (CGS)	γ, 10^{-18} (CGS)	K, 10^{-4}
0	302.95	4.34	−1.70	13.18	4.16
0.10	303.07	4.34	−1.36	8.52	4.11
0.20	302.85	4.34	−1.00	13.89	1.37
0.28	302.87	4.34	−0.24	13.98	0.08
0.30	302.93	4.34	0	11.71	0
0.35	302.90	4.34	0.07	11.57	0.01
0.45	302.70	4.34	0.38	10.92	0.25
0.80	302.17	4.34	0.77	8.41	1.35
1.30	301.42	4.34	0.97	4.78	3.84
2.00	300.50	4.34	2.78	9.76	15.24
3.00	299.12	4.34	3.35	6.81	31.85
4.50	296.98	4.34	5.20	4.96	105.37

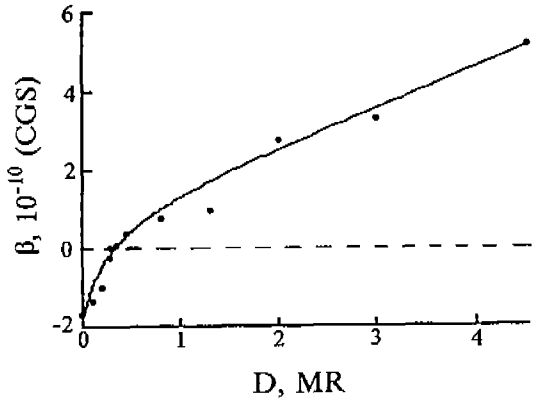

Fig. 3. The values of the Landau expansion coefficient β for different doses of γ-irradiation.

The value K for DTGSe (x=0.62) crystal becomes smaller and at D=0.3 MR it turns out to be zero. The results for parameters under irradiation clearly reveal the existence of the TCP in DTGSe (x=0.62) crystal for D=0.3 MR.

In conclusion we would emphasize that the discovered thermodynamic effect, the sensitivity of the order of the ferroelectric phase transition to the point defects induced by γ-irradiation in DTGSe crystal, was revealed for very small doses (D=0.3 MR) and did not cause smearing of the phase transitions, even for the second order one. In a small dose region the concentration of defects (dose of γ-irradiation) can be considered as an independent thermodynamic parameter like hydrostatic pressure or deuterium content, which are used to study properties of DTGSe crystal.

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