

Suppression of spontaneous deformation in triglycine sulfate crystals ($D_{0.6}H_{0.4}$) by a weak neutron flux near T_C

A. G. Lipson, D. M. Sakov, and E. I. Saunin

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russia

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It was discovered that suppression of spontaneous deformations (squeezing) occurs in partially deuterated triglycine sulfate single crystals when the crystals interact with a weak thermal-neutron flux near the Curie point. © 1995 American Institute of Physics.

It is well known¹ that low x-ray doses produce substantial radiation-induced damage in crystals of triglycine sulfate (TGS) and isomorphous compounds. In particular, this damage is seen in the change of the shape of the hysteresis loop because of the appearance of deformations of the crystal lattice and because of breaking of hydrogen bonds in the lattice. It has been determined that the x-ray doses, which give rise to radiation-induced damage in the TGS lattice, are so low that it is doubtful that the crystallographic structure of this compound can be determined correctly by the methods of x-ray crystallographic analysis. In contrast to ionizing radiation, neutron flux can produce appreciable radiation-induced damage in insulators only if the flux is high enough. This is because neutrons produce virtually no electron-hole pairs, and the defects produced by neutrons are determined by the displacement of atomic positions (nuclear recoil) in elastic and inelastic scattering and radiative capture processes.² At the same time, it is well known that in a ferroelectric phase transition through the Curie point (T_C), which is accompanied by polarization reversal of the crystal, gives rise to strongly nonequilibrium conditions. In this case the hydrogen (deuterium) atoms present in the crystal acquire a substantial mobility. Moreover, in the case of order–disorder phase transitions and partitioning of the crystals into domains, elastic deformations in the form of nonequilibrium phonons and multiphonon excitations are generated. At phase transitions of this type the chemical bonds in the crystal are in a stressed state. It thus follows that the weakest bonds (hydrogen bonds) could effectively be destroyed by even an ultralow flux not only of ionizing radiation but also of neutrons. This is possible if conditions in a ferroelectric crystal are created for effective neutron capture. For example, when a thermal neutron is captured, the nuclear binding energy that is released can be totally transferred to the lattice,^{3,4} i.e., it can be expended on breaking chemical bonds (producing radiation-induced damage). Since the typical nuclear binding energies are 7–8 MeV and the ionization energy of the chemical bonds is ~ 1 –5 eV, at least 10^6 electronic excitations could be produced with the capture of one neutron. The irradiation of ferroelectric crystals even with ultralow neutron flux in the process of a transition through T_C can therefore produce measurable electrical effects.

Such processes are especially sharply manifested in partially deuterated ferroelec-

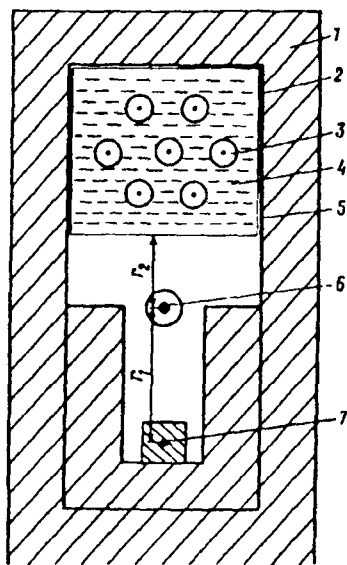


FIG. 1. Experimental arrangement. 1 — Polyethylene (Co), 2 — detector, 3 — counters, 4 — silicone oil, 5 — Cd foil, 6 — cryostat with TGS crystal, 7 — Cf^{252} neutron source.

trics (containing hydrogen and deuterium simultaneously), in which an anomalous increase in the thermal-neutron capture cross section is possible as a result of the formation in them of molecular complexes of the type⁵ $[\text{D}^+\text{H}^-]$. In connection with what we have said above, our objective in the present work was to investigate the electrical properties of the ferroelectric TGS (D, H) crystals irradiated with ultralow fluxes of thermalized neutrons near T_C and to study the capture of such neutrons in the crystal lattice.

The samples consisted of single crystals of triglycine sulfate $(\text{ND}_2\text{CD}_2\text{COOH})_3 \cdot \text{D}_2\text{SO}_4$ with total deuterium content $\sim 60\%$ ($T_C = 57.6^\circ\text{C}$). Samples with dimensions of $10 \times 10 \times 2$ mm were cut from a single-crystalline plate in the (010) direction. The temperature position and the electrical activity of the ferroelectric phase transition were monitored by the method of thermally stimulated depolarization (TSD). The samples on which ohmic contacts were deposited were secured with a measured load ($F = 100 \pm 10$ g) between two electrodes.⁶ The samples were heated and cooled in a linear regime at a rate of 0.15 K/s in the temperature interval 283–373 K. A NWI-62 block of proportional neutron counters,^{7,8} which was covered with cadmium foil and surrounded with passive shielding consisting of 15-cm-thick “neutrostop” (Co) polyethylene blocks, was used to record the neutrons. The arrangement of the experimental setup is shown in Fig. 1. A Cf^{252} source of neutrons with intensity ~ 270 neutrons/s in a solid angle of 4π was used for the experiments with neutron fluxes of different intensities (above the cosmic neutron background) and for calibrating the detector. The source, located inside a lead capsule 4 cm in diameter, was placed inside a polyethylene block, whose walls were 2.5 cm thick. The source was placed at a distance $r_1 = 10$ cm from the surface of the sample, which in turn was located at a distance $r_2 = 6$ cm from the neutron detector. For

TABLE I. Parameters of the neutron background in the apparatus in a series of experiments without (I) and with (II) a Cf^{252} neutron source at a phase transition of a TGS crystal through the Curie point.

Series	$\langle N_b \rangle$, counts/s	$\langle N_{\text{eff}} \rangle$, counts/s	$\Delta N \cdot 10^{-3}$, counts/s
I (50 cycles)	$(1.41 \pm 0.11) \times 10^{-2}$	$(1.00 \pm 0.10) \times 10^{-2}$	$-(4.1 \pm 1.1)$
II (40 cycles)	1.260 ± 0.016	1.176 ± 0.015	$-(84 \pm 20)$

Note: $\langle N_{\text{eff}} \rangle$ —average number of counts obtained in the heating—cooling cycles near T_C ; $\langle N_b \rangle$ —average number of counts obtained in the heating—cooling cycles at temperatures $T \ll T_C$ and $T \gg T_C$ (background in the control experiments); $\Delta N = \langle N_{\text{eff}} \rangle - \langle N_b \rangle$.

the control (background) experiments, the background was measured in temperature intervals outside the region of electrical activity of the TGS samples, i.e., away from T_C : 283–303 K ($T \ll T_C$) and 353–373 K ($T \gg T_C$).

As follows from Table I, the negative effect in the temperature range corresponding to the neighborhood of the Curie point is observed for both the cosmic neutron background (series I) and the Cf^{252} neutron source (series II). The absolute magnitude of the negative effect is approximately 20 times larger in the experiments with the Cf^{252} neutron source than in experiments with the cosmic background. The neutron flux from the Cf^{252} source decreases by ~ 2.0 – 2.5% as a result of interaction with the TGS crystal near T_C .

At first glance, this result appears to be paradoxical, since in the absence of a moderator the neutron flux I incident on the crystal must decrease with distance as $I \sim r^{-2}$. When large moderator masses are present, however, this law does not hold (Fig. 2). In this case three sections can be separated on the plot of the function $N(r)$: 1) $r \geq 30$ cm (neutron source outside the polyethylene shielding: $N \sim r^{-2}$); 2) $10 < r < 30$ cm (source inside the shielding $N \sim r^{-1}$), and 3) $r < 10$ cm, $N \sim r^{-1/n}$ (where $2 < n < 3$). This dependence $N(r)$ is determined by the fact that the neutrons thermalized inside the polyethylene shielding can repeatedly cross (several tens of times) the same plane (crys-

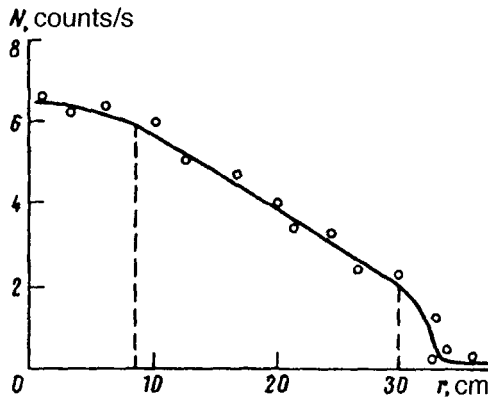


FIG. 2. Neutron counting rate as a function of source—detector distance inside the polyethylene shielding.

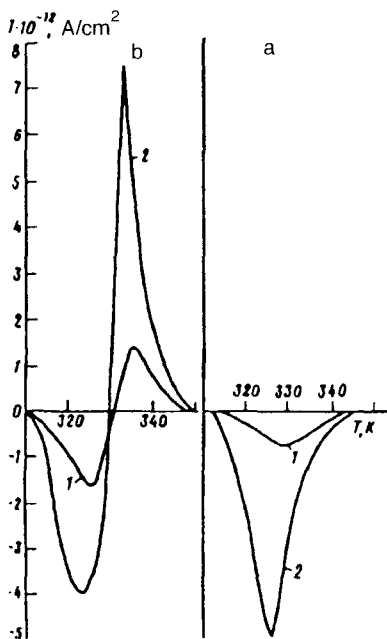


FIG. 3. a — TSD spectra of a TGS sample with cooling under the conditions of the cosmic neutron background (curve 1) and with a Cf^{252} neutron source (curve 2); b — same for the case of heating.

tal), undergoing internal reflections from the polyethylene walls.⁹ This means that a “field” of thermal neutrons moving randomly in different directions is produced inside the shielding in the space between the source and the detector (source and crystal).¹⁰ Taking into account the total surface area of the sample ($S_{\text{sample}} = 2.8 \text{ cm}^2$), the number of thermalized neutrons crossing the sample per unit time in the given geometry is equal to ~ 20 neutrons/s, of which almost one third are captured in the crystal. It thus follows that the neutron capture cross section in TGS crystals near T_C must be at least three orders of magnitude larger ($\sim 700 \text{ b}$) than for hydrogen in a TGS crystal.

According to Fig. 3 the capture of thermalized neutrons in a TGS crystal near T_C results in a substantial change in the TSD spectra as compared with the similar spectra obtained for the same crystal in the absence of the Cf^{252} source (cosmic-background conditions). First, the intensity of the TSD signal (2) for the irradiated samples is markedly higher. Second, for the samples 2 the peaks of the TSD current are shifted during heating and cooling by 3.5 K at low temperatures. This indicates that T_C is correspondingly lower than in the samples subjected to heat-cycling under the conditions of the cosmic neutron background (sample 1). Third, the activation energy of the TSD process for sample 2, calculated by the Garlik–Gibson method,⁶ is $(\delta_{\text{cool}})_2 = 1.3 \pm 0.1 \text{ eV}$ on cooling and $(\delta_{\text{heat}})_2 = 1.5 \pm 0.1 \text{ eV}$ on heating, while for sample 1 $(\delta_{\text{cool}})_1 = 1.0 \pm 0.1 \text{ eV}$ and $(\delta_{\text{heat}})_1 = 1.2 \pm 0.1 \text{ eV}$, respectively; i.e., for the irradiated samples the activation energy of polarization reversal in a TGS crystal is approximately 0.3 eV higher. We note that

irradiation of the crystal with a Cf^{252} neutron source before the transition $T < T_C$, and also at $T > T_C$ does not change the TSD spectra (in contrast to TGS samples irradiated with γ rays¹). After the TGS crystal is irradiated near T_C and after the subsequent transition through T_C in the absence of the source, the TSD spectrum is identical to the spectrum obtained under cosmic-background conditions. The change in the electrical activity of a TGS crystal irradiated with low thermal-neutron fluxes therefore occurs only at the moment of irradiation and only near T_C .

We shall now examine the possible reasons for the observed changes in the electrical activity of a TGS crystal irradiated with a weak flux of thermal neutrons. The shift in T_C in ferroelectric crystals at low temperatures by the amount ~ 3.5 K indicates that during the measurements the crystal becomes mechanically squeezed between the electrodes.¹¹ This effect is due to the partial suppression of spontaneous deformations in the crystal, resulting in the suppression of spontaneous polarization in the region $T > T_C$, as compared with the "free" crystal; i.e., the ferroelectric region decreases. The suppression of spontaneous deformation is evidently due to the conversion of part of the elastic energy of domain walls into the energy of plastic deformation which accompanies the interaction of the TGS crystal with the thermal neutron flux, since under cosmic-background conditions the crystal remains "free." The energy of plastic deformation which is released in such a process is expended on dielectric losses due to the friction between the domains, on the generation of charged dislocations in the skin layer of the TGS crystal, on microcracks, etc. This increases the surface charge in the crystal. The latter process involves an increase in the electrical activity of the sample.¹² The intensity of the TSD signal increases in the process and the activation energy of polarization reversal increases as a result of an increase in the mechanical resistance to switching of domains as the number of structural defects in the TGS crystal increases. The process of polarization reversal in a TGS crystal in the usual case (no irradiation) is determined by the transfer of hydrogen from the COOH group of the glycine ion to a dipolar ion $(\text{ND}_2)\text{D}^+\text{CH}_2\text{COO}^- : ((\text{ND}_2)\text{D}^+\text{CD}_2\text{COO}^-)(\text{ND}_3^+\text{CDCOOH})_2\text{SO}_4^{2-}$. As a result, the nitrogen atoms of the glycine groups and the glycine ions are displaced and reordered, which results in the formation of a polarized state. In the case of irradiation, i.e., when excess energy of plastic deformation is present near a domain wall, the short hydrogen bond COOH in the $(\text{ND}_2)\text{D}^+\text{CD}_2\text{COO}^-$ group can break. In the process a hydrogen atom becomes mobile and can cross over to the $(\text{ND}_2)\text{D}^+$ group, where the complex $[\text{D}^+\text{H}^-]$ apparently forms. An additional negative charge COO^- , which increases the polarization of the sample, also forms. The energy required to break a short hydrogen bond is $E_H = 0.3$ eV/atom. This energy corresponds to the difference $\delta_2 - \delta_1$, i.e., the difference in the activation energies of the polarization reversal processes in irradiated and unirradiated crystals.

It is easy to show that the energy required to increase the electrical activity of TGS under irradiation can be provided by the capture of thermal neutrons that cross the crystal. The average increase in the charge in irradiated crystals, calculated from Fig. 2a, is $\Delta Q = 8 \times 10^{-10}$ C/cm²·s, which corresponds to $n \sim 2 \times 10^7$ elementary charges additionally formed in the crystal under irradiation. The energy required to form this number of charges, taking into account the arguments presented above, is $W_e = n_e E_H$, where E_H is the energy of a short hydrogen bond in TGS. We thus have $W_e \approx 6 \times 10^6$ eV/s. At the same

time, as shown above, I_n neutrons are captured per second in the crystal on passing through T_C : $I_n \approx 6$ neutrons/s. Assuming that the capture of neutrons in the domain walls occurs nonradiatively (by analogy with the Mössbauer effect^{3,13}) as the energy of the captured radiation is transferred to the lattice ($E_\gamma \geq 2.22$ MeV), we obtain for the total power released as a result of bombarding the crystal with neutrons, $W_n \geq 1.32 \times 10^7$ eV/s. Clearly, $W_n > W_e$. The energy released inelastically as a result of the capture of thermal neutrons from the Cf²⁵² source is therefore sufficient for producing the experimentally observed "excess" charge in the irradiated TGS samples.

The suppression of the spontaneous deformation and possibly the increase in the cross section for the capture of thermal neutrons can be attributed to the anomalously high constant of the interaction between phonons in the TGS lattice and the angular momenta of the quasimolecule HD. This interaction constant is more than two orders of magnitude higher than the analogous constant for H₂ and D₂ molecules,¹⁴ because of the large asymmetry of the HD molecule, in which the center of mass and the center of interaction of the charges are shifted relative to one another by 0.12 Å. In this case the complexes [D⁺H⁻] formed in TGS near T_C are essentially sinks for elastic deformation energy. The number of such sinks increases rapidly as a result of neutron bombardment, which accounts for the suppression of spontaneous deformation.

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