

## Band structure and optical spectra of ferroelectric triglycine sulphate

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First-principal calculations of the band structure, density of electronic states, and dielectric functions of the triglycine sulphate crystal (TGS) together with the corresponding experimental dielectric functions in the range of 4–10 eV have been presented. Calculations have been performed in the frame of density functional theory using the CASTEP code. The experimental dielectric functions  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  have been obtained for different temperatures by ellipsometry using the synchrotron radiation source BESSY II. The theoretical dielectric functions  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  of TGS crystal agree satisfactorily with corresponding experimental dependencies. The character and magnitude of temperature changes of dielectric functions in the vicinity of phase transition point depend on the crystal orientation and photon energy. The greatest maximum-like temperature changes of dielectric functions observed at the phase transition point are detected for the photon energy  $\omega \approx 9.5$  eV.

*Keywords:* Ferroelectrics; TGS; Band structure; Dielectric function

### 1. Introduction

The triglycine sulphate crystal (TGS),  $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ , is a known ferroelectric and belongs to the monoclinic space group  $P2_1$ . Above the transition temperature it becomes paraelectric of the monoclinic group  $P2_1/m$  [1–4]. Two formula units are in the crystal unit cell of TGS. The structure of this crystal is a complicated arrangement of quasi-molecular glycine complexes, sulphate anions, and hydrogen bonds O–N...–O and N–H...–O. Parameters of the TGS crystal unit cell in ferroelectric phase are the following:  $a = 9.419 \text{ \AA}$ ,  $b = 12.647 \text{ \AA}$ ,  $c = 5.727 \text{ \AA}$ ,  $\beta = 110.32^\circ$  [4]. The spontaneous polarization vector  $P_s$  of TGS crystal is parallel to

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the two-fold axis of symmetry and is formed mainly by the proper position of the  $\text{NH}_3^+$  subgroup of the glycine-1 group.

The study of optical characteristics of TGS crystals in the range of electronic excitations can be particularly useful for the investigation of relations between the peculiarities of electronic structure and the ferroelectric state formation. Physical properties of TGS crystals were widely studied experimentally and theoretically. First measurement of the partially polarized reflectance spectra of TGS crystals in the range of 4–22 eV were done using the Lyman discharge light source with the relatively low accuracy of 10–30% [5]. First-principal calculations of the electronic band structure of TGS crystals were performed in our previous article [6].

In the present article, the results of theoretical first-principal calculations of the electronic band structure and optical spectra of TGS crystal have been presented on the basis of our study [6] together with the measurements of its optical properties in the range of 4–10 eV performed using synchrotron radiation at different temperatures.

## 2. Methods of investigation

Calculations of the band energy dispersion  $E(k)$ , density of electronic states (DOS), and dielectric functions  $\varepsilon(\omega)$  of TGS crystal have been performed in a frame of the density functional theory (DFT) using the CASTEP code [7]. Calculations were carried out using a plane-wave basis set with the cut-off energy of 340 eV, ultrasoft pseudopotentials [8], and within a framework of the generalized gradient approximation (GGA) for the exchange and correlation effects [9]. Before the main calculations of the band structure and related properties, the optimization (relaxation) of the unit cell parameters and the atomic coordinates in the crystal was performed. Band structure of the crystal was calculated for 23  $k$ -points of the Brillouin zone (BZ).

Measurement of the pseudo-dielectric function  $\varepsilon = \varepsilon' + i\varepsilon''$  of TGS crystals have been done by spectroscopic ellipsometry using the synchrotron-ellipsometer [10, 11] attached to the 3 m Normal Incidence Monochromator (NIM) of the Berlin Electron Storage ring for Synchrotron radiation BESSY II. Measurements were done in the spectral range of 4.0–9.9 eV with the resolution of 0.02 eV. The angle of incidence was  $\sim 68^\circ$ , while the polarization of the incident beam was chosen  $\sim 20^\circ$  tilted with respect to the plane of incidence during the measurements. A  $\text{MgF}_2$  polarizer and rotating analyzer, respectively, ensured a 99.998% degree of polarization.

The cleaved (perpendicularly to  $Y$ -direction) and mechanically polished surfaces of TGS crystal were used for measurement.

## 3. Results and discussion

Optimization of the initial experimental atomic coordinates of TGS crystal leads to the corresponding relative changes not exceeding 2%. However, in the case of the ultrasoft potentials used a relative increasing of the unit cell parameters  $a$ ,  $b$ , and  $c$  by the magnitude of 3–5% takes place after this optimization.

The study of the band structure of TGS crystal has revealed the flat or low dispersive wave vector dependence of the electron energy  $E(k)$  [6] corresponding to the weak inter-cell electronic interactions. The energy band gap of the TGS crystal was found to be indirect and corresponds to the optical transitions between  $\Gamma$  and D points of the BZ [6]. This value,  $E_{\text{gi}} = 4.65$  eV, is close to the experimental one,  $E_{\text{gi}}^{(e)} = 4.97$  eV [12], when the scissor factor of 0.9 eV is used.

The Mulliken population analysis of the TGS crystal have revealed a greater covalent character of chemical bonds in the glycine group of the unit cell than that found in the sulphate one [12].

Analysis of the DOS has revealed that the upper part of the valence band,  $-3.0$  eV to  $0.5$  eV, is mainly (95%) of  $p$ -character (figure 1). In the valence band energy range,  $-10.0$  eV to  $-3.0$  eV, the part of  $p$ -states is equal to about 70%, whereas in the range of  $-23.0$  eV to  $-11.0$  eV the part of  $p$ -states is about 20% (figure 1). The lower part of the conduction band,  $4.0$ – $6.0$  eV, is also mainly of  $p$ -character (80%). Both glycine and  $\text{SO}_4$  groups give input into the density of  $p$ -states in the upper part of the valence band,  $-3.0$ – $0.5$  eV, whereas the lower part of the conduction band,  $4.0$ – $6.0$  eV, is formed predominantly (98%) by the states of three glycine groups (figure 2). It was also found that in this region, the DOS for three different glycine groups are shifted in energy, that testifies for the antibonding character of the corresponding electronic states.

Analysis of the DOS by chemical elements has revealed that the predominant part of DOS (92%) in the range of  $-3.0$ – $0.5$  eV is formed by the  $p$ -states of oxygen (figure 2). In particular, the highest valence energy states at  $E = -0.2$  eV are formed by the oxygen of  $\text{SO}_4$ -groups and glycine-2 group. The lower part of the conduction band,  $4.0$ – $6.0$  eV, is formed by carbon (53%), oxygen (30%), and hydrogen (16%). The part of the hydrogen electronic states in the range of  $6.0$ – $11.0$  eV is the greatest and is equal to about 45%. The conduction band of the crystal is a mixed one

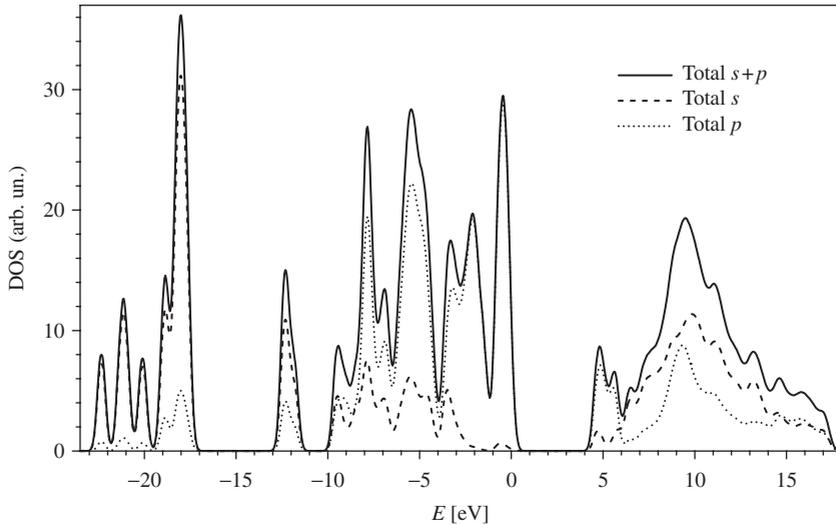


Figure 1. Densities of electronic states (total,  $s$ , and  $p$ ) of TGS crystal in the ferroelectric phase.

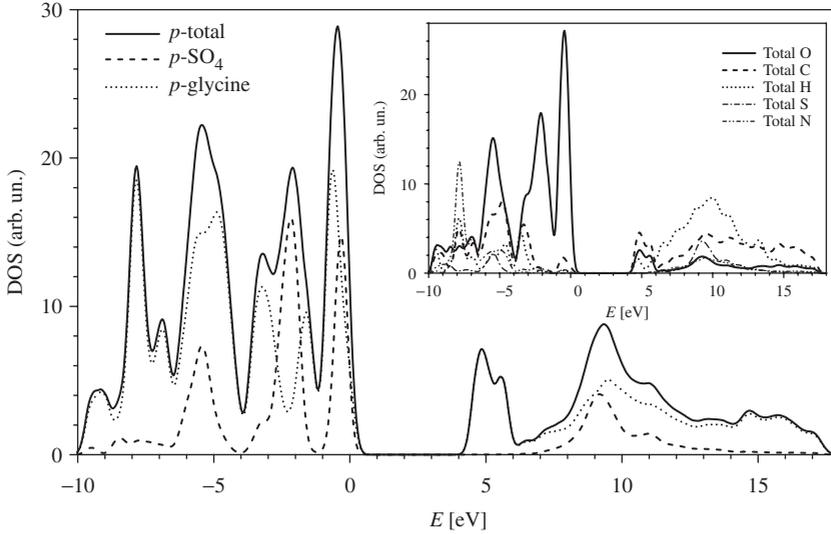


Figure 2. Densities of electronic  $p$ -states (total,  $\text{SO}_4$ , and glycine) of TGS crystal at ferroelectric phase. In the insertion, the total densities of electronic states for atoms O, C, H, S, and N.

regarding to the character ( $s$ -, and  $p$ -type) and origin (chemical elements) of the electronic states.

The pseudo-dielectric function  $\langle \varepsilon \rangle = \langle \varepsilon' \rangle + i \langle \varepsilon'' \rangle$  of the TGS crystal experimentally obtained for one of the possible relative ‘light–sample’ orientation and all three theoretical functions  $\varepsilon''(\omega)$  for the principal directions of the optical indicatrix are presented in figure 3. The experimentally obtained  $\langle \varepsilon'' \rangle(\omega)$  dependencies are characterized by the clear spectral band in the range of 6.6–8.2 eV and by the increase in the range of 9.0–10.0 eV (figure 3). The spectra of pseudo-dielectric functions  $\langle \varepsilon' \rangle(\omega)$  and  $\langle \varepsilon'' \rangle(\omega)$  depend significantly on the cut orientation of the sample surface. The most pronounced peak of  $\langle \varepsilon'' \rangle(\omega)$  at the photon energy  $\omega = 7.3$  eV is observed for the planes of incidence  $YX$  and  $ZX$  [6]. For the plane of incidence  $YZ$  this peak is smaller (figure 3). The magnitudes of pseudo-dielectric function  $\varepsilon'(\omega)$  at  $\omega = 4$  eV agree within 10% with the square of refractive indices of TGS crystals [13].

The theoretical long-wave edge of fundamental absorption of TGS crystal determined by the  $\varepsilon''(\omega)$  dependence is close to the experimental one when the scissor factor of 0.9 eV is used, that is typical for the DFT-based calculations. Analysis of the band structure has shown that the strong spectral band of  $\varepsilon''(\omega)$  with maximum at  $\omega = 7.3$  eV corresponds to the direct optical transitions at  $\Gamma^-$ ,  $Y^-$ ,  $B^-$ , and  $E^-$  points [6]. These transitions are associated with the valence  $p$ -states of oxygen and, predominantly, with the conducting states of hydrogen and carbon (figure 2). Great anisotropy of the dependence  $\varepsilon''(\omega)$  in the region of maximum at  $\omega = 7.3$  eV (figure 3) and peculiarities of the spatial orientation of the crystal’s fragments in the unit cell support a suggestion that the mentioned valence  $p$ -states of oxygen are associated with  $\text{SO}_4$  groups, whereas the conduction band states of hydrogen and carbon ( $s$ -states) are mainly formed by the glycine-1.

Similar analysis of the experimental and theoretical dielectric functions  $\varepsilon''(\omega)$ , band dispersion, and densities of states for TGS crystal gives possibility to assign the

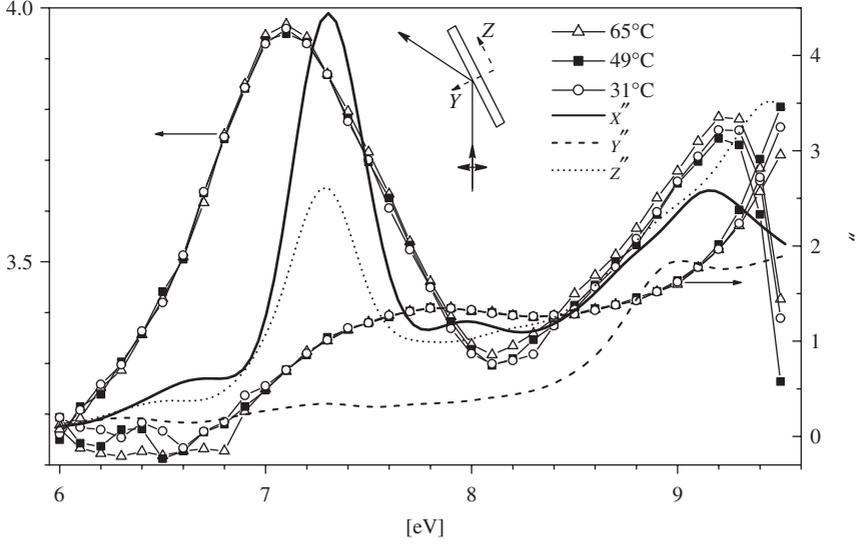


Figure 3. Pseudo-dielectric functions  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  of TGS crystal experimentally obtained for the temperatures 31°C, 49°C, and 65°C (points + lines) and the theoretical functions  $\epsilon''(\omega)$  for three principal directions  $X$ ,  $Y$ ,  $Z$  of optical indicatrix (lines).

experimental maxima of  $\epsilon''(\omega)$  at 8.35 eV and 9.55 eV to the transitions between the oxygen valence  $p$ -states, probably partially delocalized, and lower lying delocalized states of the conduction band ( $\omega > 6.0$  eV).

For the TGS samples of  $Y$ -cut and  $YZ$  incidence plane ( $YZ$ -geometry), the extrema of temperature dependencies of the real ( $\chi'_{\text{rel}}$ ) and imaginary ( $\chi''_{\text{rel}}$ ) parts of the susceptibility,  $\chi = (\epsilon - 1)$ , of TGS crystal take place at the phase transition point for the energies near  $\omega = 9.5$  eV (figure 4). The temperature dependency of  $\chi''_{\text{rel}}(T)$  in the vicinity of phase transition point demonstrates the critical-like behaviour,  $\chi'' \sim (T - T_c)^{-\nu}$ , similar to the corresponding known dependency of static dielectric permittivity caused by the domain-like relaxation of TGS crystal. The increase of the relative susceptibility  $\chi''(T)/\chi''(65^\circ\text{C})$  at the temperature of 49°C is equal to the considerable magnitude of 17%, that is approximately twice greater than the similar value for the temperature of 31°C (figure 4). So, the probability of optical transitions near the energy of 9.5 eV at the temperature of ferroelectric phase transition (49°C) is greater than that for the any other temperature around this point. It is interesting that the character of the temperature dependencies  $\chi_{\text{rel}}(T)$  obtained (figure 4) is very similar to the temperature dependence of the relative optical path difference in the spectral range of the crystal's transparency ( $\omega = 1.96$  eV) induced by the constant electric field along the polar  $Y$ -direction [14].

One has to take into account that the extremum-like temperature dependency of dielectric permittivity and susceptibility of TGS crystal takes place only for  $YZ$ -geometry of experiment (figure 3), for which the  $Z$ -component of electric vector of light is considerable. For the geometries  $YX$  and  $ZX$  of experiment this  $Z$ -component of electric vector is relatively smaller. Taking into account the density of electronic states (figure 2), one can suppose that the temperature dependency presented in figure 4 is associated with the electronic excitation of  $\text{O-H}\cdots\text{O}$  bonds directed mainly along  $Z$ -axis between the glycine-2 and glycine-3 groups. At the

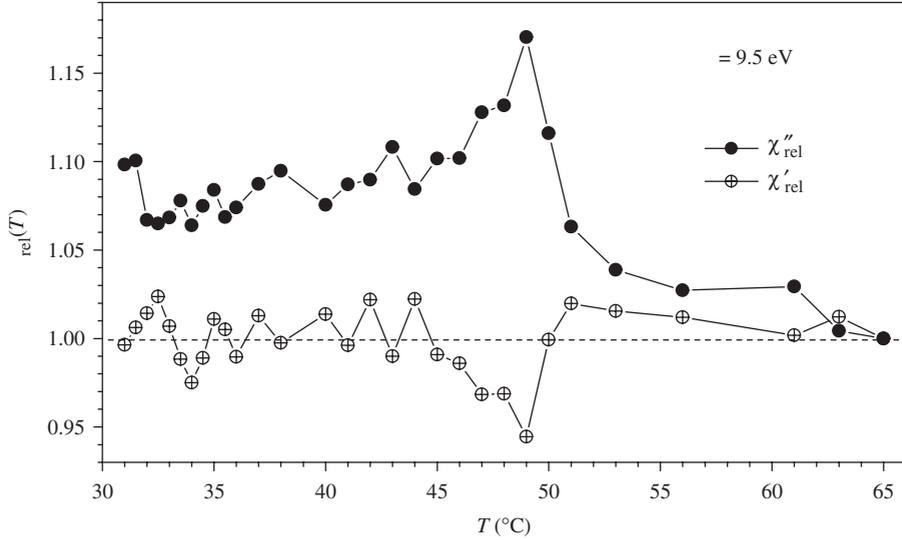


Figure 4. Temperature dependencies of the real ( $\chi'_{rel}$ ) and imaginary ( $\chi''_{rel}$ ) parts of the relative susceptibility  $\chi(T)/\chi(65^\circ\text{C})$  for YZ-geometry of TGS crystal and photon energy  $\omega=9.5\text{ eV}$ .

temperature of ferroelectric phase transition, the hydrogen atoms of the O–H...O bonds are bound with neighbouring O atoms with the smallest strength. Then the electron population of the H atoms is probably the highest, and, therefore, the probability of the corresponding electronic excitations is the greatest.

#### 4. Conclusions

The upper part of the valence band of TGS crystal,  $-3.0$ – $0.5\text{ eV}$ , is mainly (95%) of  $p$ -character and oxygen origin. The electronic states of the lower part of the conduction band,  $4.0$ – $6.0\text{ eV}$ , are also mainly the  $p$ -states (80%) of three glycine groups, but are of the antibonding character.

The strong spectral band of the dielectric function  $\varepsilon''(\omega)$  with maximum at  $\omega=7.3\text{ eV}$  corresponds to the direct optical transitions in the  $\Gamma$ -,  $Y$ -,  $B$ -, and  $E$ -points of BZ.

Extrema of the temperature dependencies of dielectric susceptibility (permittivity) taking place at the phase transition point for the energy  $\omega=9.5\text{ eV}$  demonstrate the critical-like behaviour,  $\varepsilon'' \sim (T - T_c)^{-\nu}$ , similar to the corresponding known dependencies of the dielectric permittivity for low frequencies ( $\sim 1\text{ kHz}$ ) and the relative optical path difference induced by the static electric field along the polar  $Y$ -direction of TGS crystal.

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