# Physical origin of the dynamical central peak in ferroelectric triglycine sulfate

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The picosecond time-resolved spectroscopy is carried out to clarify the physical origin of the central peak that has been reported in uniaxial ferroelectric triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS). An ultraslow relaxational mode with a relaxation time $\tau = 5-8$ $\mu$sec is reported as a real-time signal intensity $I(t)$ and is assigned to a thermal relaxational mode. This assignment is based on the fact that the diffusion constant evaluated from $\tau$ agrees well with the thermal diffusivity measured by heat-pulse method. The discovered mode, the thermal relaxational mode, is proved to be the physical origin of the reported central peak of TGS from the anisotropic anomalous behavior of the signal intensity at time origin $I(0)$. [S0163-1829(99)00201-5]

The peak with zero-frequency shift has been found both in quasielastic neutron- and light-scattering spectra.[1,2] This peak is called a central peak and the mode causing the central peak is referred to a central mode. Especially the central peak that shows the anomalous behavior near the structural phase-transition temperature is very attractive because the peak gives us important information on the dynamical mechanism of the phase transition. The light-scattering method, which has a spectral resolution better than the neutron-scattering method, has been utilized extensively to study this type of central peak.[2] The direct measurement of the spectral width of the central peak, the inverse of which is the characteristic time of the central mode, is essential to determine the physical origin of the central peak and to extract information on the phase-transition dynamics from the peak. However, the observed central peak is sometimes too narrow to measure the spectral width even in the light-scattering method due to the spectral resolution limit of spectrometer.

Miyakawa and Yagi found a narrow central peak in order-disorder-type uniaxial ferroelectric triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) by a 90° Brillouin scattering experiment.[3] The peak intensity of the central peak shows anisotropic anomalous behavior; a $\lambda$-type anomaly is present along the *c* axis but no anomaly is present along the polar *b* axis. They could not measure the spectral width of the central peak due to the spectral resolution limit of Fabry-Pérot interferometer (about 1 GHz), which yielded two different interpretations for the physical origin of the central peak. One is a thermal relaxational mode and the other is a polarization relaxational mode.

Miyakawa and Yagi attributed the physical origin of the central peak of TGS to a thermal relaxational mode (temperature or entropy fluctuation).[3] They interpreted that the anomaly of the central peak is associated with that of heat capacity. This interpretation contains a problem, because heat capacity is a scalar (isotropic) quantity and cannot show anisotropic anomalous behavior. Some other reasonable explanation is needed in order to insist that the physical origin of the central peak is a thermal relaxational mode.

Tokunaga proposed that the physical origin of the central peak of TGS is a polarization relaxational mode (polarization fluctuation).[4] This proposal seems to be fine at first glance, since the anisotropic anomaly of the polarization fluctuation seems to be explained simply by a depolarization field effect (suppression of the polarization fluctuation along the polar *b* axis due to depolarization field).[5] However, it is required to confirm experimentally that the characteristic time of the central peak is the same as the relaxation time of the polarization fluctuation.

It is apparent that the measurement of the spectral width of the central peak is inevitable to determine the physical origin of the central peak of TGS, the thermal or the polarization relaxational mode. In order to measure the spectral width, the authors used a time-resolved spectroscopy called impulsive stimulated scattering (ISS), which is known to be an excellent experimental method with which to realize a spectral resolution higher than 1 GHz.[6–8] In ISS, coherent modes (acoustic phonon and relaxational mode) are excited impulsively by crossing two light pulses inside the sample and their real-time behavior is probed by pulse or cw laser beam. If a picosecond pulse laser is used for mode excitation, one can easily obtain a time resolution of 1 nsec. The time region longer than 1 nsec corresponds to the frequency region lower than 1 GHz, which means that ISS can realize the spectral resolution much higher than 1 GHz of the Fabry-Pérot interferometer. The purpose of the present paper is to clarify the physical origin of the central peak reported in TGS. For this purpose, the coherent modes are excited and are observed in a time region much longer than 1 nsec by the use of ISS technique.

Two TGS samples were prepared for the present experiment. The *b* plate sample of size $5.4 \times 7.7 \times 0.6$ mm$^3$ was used to study the modes with the wave vector $\mathbf{q} \| a^*$ axis and with the $\mathbf{q} \| c$ axis. The *c* plate sample of size $2.5 \times 5.5 \times 0.8$ mm$^3$ was used to study the modes with $\mathbf{q} \| b$ axis. The ferroelectric transition temperature $T_c$ was determined to be 48.5 °C from the measurement of the dielectric constant along the *b* axis. A $Nd^{3+}$:$LiYF_4$ (Nd:YLF) pulse laser (Quantronix 4217) was used for the excitation of modes at the wavelength $\lambda_E = 1053$ nm. The mode-locking frequency and *Q*-switching repetition were 82 MHz and 400 Hz, respectively. A single pulse of 110 $\mu$J and 60 psec emitted from the laser was passed through a Glan laser prism to prepare two excitation pulses. These excitation pulses were polarized vertically and crossed inside TGS samples with a

 

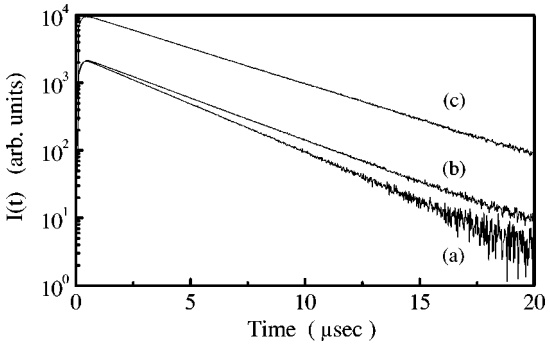


FIG. 1. The real-time signal intensity $I(t)$ caused by the relaxational mode with $|\mathbf{q}|=7.5\times10^3$ cm$^{-1}$ at $T=44.6\,^\circ$C. (a) $\mathbf{q}\|a^*$, (b) $\mathbf{q}\|b$, and (c) $\mathbf{q}\|c$ axes.

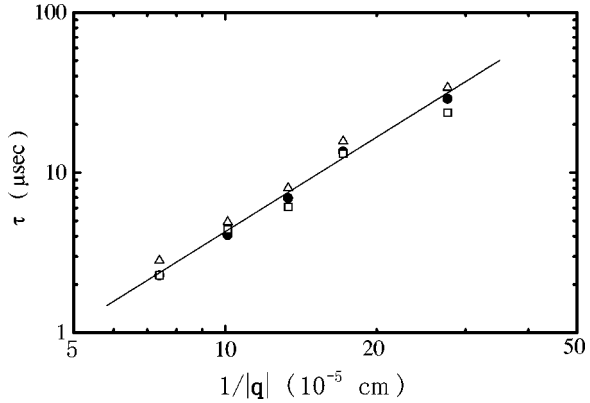


FIG. 2. The relaxation time $\tau$ as a function of $|\mathbf{q}|^{-1}$ at $T=44.6\,^\circ$C; $\mathbf{q}\|a^*$ (squares), $\mathbf{q}\|b$ (closed circles), and $\mathbf{q}\|c$ (triangles) axes. The solid line expresses the relation of $\tau\propto|\mathbf{q}|^{-2}$.

crossing angle $\theta$, which excites impulsively the spatially coherent modes (acoustic phonon and relaxational mode) with a wave vector $\mathbf{q}$ determined uniquely by the crossing geometry. The vector $\mathbf{q}$ lies in a plain formed by two paths of the excitation pulses and is perpendicular to the bisector of $\theta$. The magnitude of $\mathbf{q}$ is given by a formula $|\mathbf{q}|=(2\pi/\lambda_E)2\sin(\theta/2)$. In order to probe the excited modes, the vertically polarized probe beam from a cw $Ar^+$ gas laser (Spectra-Physics BeamLok 2060) with the wavelength $\lambda_P=514.5$ nm was focused into the sample with an angle $\theta_B$ satisfying the Bragg diffraction condition (phase matching condition). The angle $\theta_B$ was calculated from a formula; $\lambda_P/\sin(\theta_B/2)=\lambda_E/\sin(\theta/2)$. The Bragg-diffracted probe beam was detected by a photomultiplier tube (Hamamatsu R1636) and was stored in a digitizing oscilloscope (Tektronix TDS540A) as a real time signal.

The modes, the wave vectors $\mathbf{q}$, which are parallel to the $a^*$, $b$, and $c$ axes, respectively, were excited in the present ISS experiment. The value of $|\mathbf{q}|$ was $7.5\times10^3$ cm$^{-1}$, as the crossing angle $\theta$ was set to be 7.2°. Two kinds of modes were detected along each $\mathbf{q}$ direction. One is a longitudinal acoustic phonon vibrating in a time range of 0–10 nsec, which has already reported in Ref. 8. In addition to this mode, a new relaxational mode was discovered with an ultraslow relaxation time of about 10 $\mu$sec (with a frequency region of about 100 kHz, realizing a spectral resolution much higher than the 1 GHz of a Fabry-Pérot interferometer). Figure 1 shows a typical real-time signal intensity $I(t)$ caused by the discovered relaxational mode at $T=44.6\,^\circ$C on a semilogarithmic scale. Since the longitudinal acoustic phonon attenuates completely at about 10 nsec, it does not appear in this figure. The intensity $I(t)$ clearly shows a simple exponential decay, indicating that the relaxational mode has a single relaxation time $\tau$, $6.1\pm0.1$, $6.9\pm0.1$, and $8.0\pm0.1$ $\mu$sec along the $a^*$, $b$, and $c$ axes, respectively.

In order to clarify the physical origin of the relaxational mode, $|\mathbf{q}|$ dependence of $\tau$ was investigated at $T=44.6\,^\circ$C. For this purpose, the intensity $I(t)$ was studied with the crossing angles $\theta$ of 3.5°, 5.6°, 7.2°, 9.5°, and 13.0°, corresponding to $|\mathbf{q}|$ of $3.6\times10^3$, $5.8\times10^3$, $7.5\times10^3$, $9.9\times10^3$, and $13.5\times10^3$ cm$^{-1}$, respectively. The relaxation time $\tau$ evaluated from $I(t)$ is plotted in Fig. 2 as a function of $|\mathbf{q}|^{-1}$ on a logarithmic scale. It is obvious that $\tau$ is proportional to $|\mathbf{q}|^{-2}$ along each $\mathbf{q}$ direction. This proportionality implies that the discovered relaxational mode can be assigned to a diffusive process with a diffusion constant $D_{ISS}=1/(\tau|\mathbf{q}|^2)$. To obtain the more detailed information on this diffusive process, the temperature dependence of $I(t)$ was measured at fixed $|\mathbf{q}|=7.5\times10^3$ cm$^{-1}$. After $\tau$ was obtained from $I(t)$, $D_{ISS}$ was calculated by the use of the expression $D_{ISS}=1/(\tau|\mathbf{q}|^2)$. The temperature dependences of $\tau$ and $D_{ISS}$ are presented in Figs. 3 and 4, respectively. For later discussion, the real-time signal intensity at time origin $I(0)$ is also evaluated by extrapolating $I(t)$ to time origin and is plotted in Fig. 5 as a function of temperature. A dominant anomaly of $D_{ISS}$ is seen in Fig. 4 along the $a^*$ and $c$ axes, but no anomaly is seen along the $b$ axis. The temperature dependence and the anisotropy of $D_{ISS}$ are almost the same as those of the thermal diffusivity $D_{th}$ measured by heat-pulse method under the open circuit condition (the condition of electric displacement $D=0$).[9] Therefore, it is concluded that $D_{ISS}$ is the same physical quantity as $D_{th}$ and that the observed relaxational mode corresponds to a thermal diffusion process, that is, to a thermal relaxational mode. The present ISS is essentially the impulsive stimulated thermal scattering (ISTS), because the excitation of the thermal relaxational mode arises from the energy absorption of the excitation pulses into O-H and/or C-H vibration overtones. This type of absorption has been observed in many

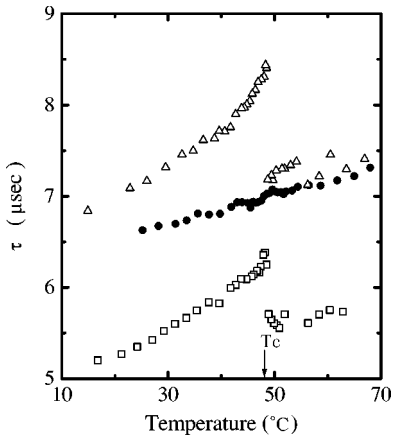


FIG. 3. The temperature dependence of the relaxation time $\tau$ of the relaxational mode with $|\mathbf{q}|=7.5\times10^3$ cm$^{-1}$; $\mathbf{q}\|a^*$ (squares), $\mathbf{q}\|b$ (closed circles), and $\mathbf{q}\|c$ (triangles) axes.

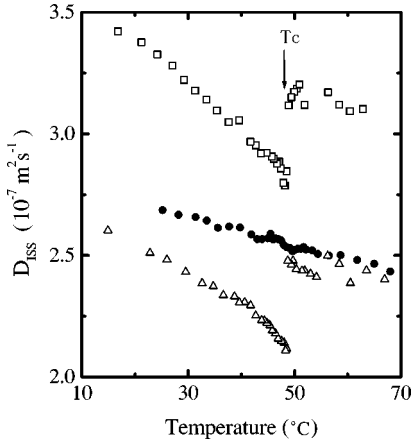


FIG. 4. The temperature dependence of the diffusion constant $D_{ISS}=1/(\tau|\mathbf{q}|^2)$ of the relaxational mode with $|\mathbf{q}|=7.5\times10^3$ $cm^{-1}$; $\mathbf{q}\|a^*$ (squares), $\mathbf{q}\|b$ (closed circles), and $\mathbf{q}\|c$ (triangles) axes.

organic materials at an excitation wavelength of 1064 nm.[6,10]

Using the result of $I(0)$ shown in Fig. 5, we will prove that the physical origin of the central peak found by Brillouin scattering is the thermal relaxational mode. It is apparent from this figure that a large anomaly of $I(0)$ is present along the $c$ axis but no clear anomalies of $I(0)$ are present along the $a^*$ and $b$ axes. The theoretical formulation of $I(0)$ for a thermal relaxational mode has been already obtained and is expressed approximately as[11,12]

$$I(0)\propto\left(\frac{\alpha}{C_X}\right)^2. \tag{1}$$

Here $\alpha$ and $C_X$ are the thermal expansion coefficient and the specific heat at constant stress $X$, respectively. The temperature dependence of $(\alpha/C_X)^2$ is evaluated from the reported values of $\alpha$ (Refs. 13 and 14) and $C_X$ (Ref. 15) and is plotted in Fig. 5 by a curved line. The coincidence between the observed $I(0)$ and the curved lines is excellent. As the thermal expansion coefficient $\alpha$ has the anisotropic nature and shows the anomaly much stronger than $C_X$,[13–15] it is concluded that the temperature dependence and the anisotropic behavior of $I(0)$ are explained mainly by those of $\alpha^2$.

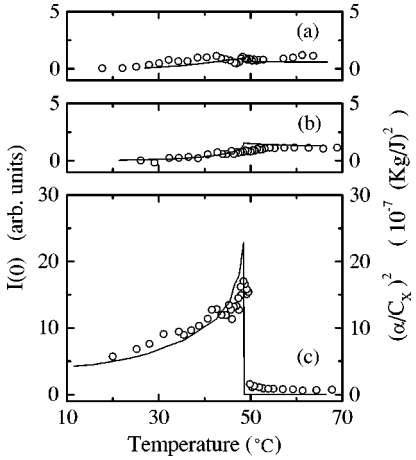


FIG. 5. The temperature dependence of the real-time signal intensity at time origin $I(0)$ caused by the thermal relaxational mode with $|\mathbf{q}|=7.5\times10^3$ $cm^{-1}$ (circles) and the temperature dependence of the calculated value of $(\alpha/C_X)^2$ (curved lines); (a) $\mathbf{q}\|a^*$, (b) $\mathbf{q}\|b$, and (c) $\mathbf{q}\|c$ axes.

Miyakawa and Yagi found a central peak in TGS by 90° Brillouin scattering and calculated the Landau-Placzek ratio $R_{LP}=I_R/(2I_B)$ from their experimental results.[3] Here $I_R$ and $I_B$ are the integrated intensities of the central peak and Brillouin peak, respectively. They reported that the temperature dependence of $R_{LP}$ shows a λ-type anomaly along the $c$ axis but it does not show any anomaly along the polar $b$ axis. This temperature dependence and the anisotropic behavior of $R_{LP}$ are very similar to the present results shown in Fig. 5, which gives us the idea that the physical origin of the central peak must be the thermal relaxational mode. Miyakawa and Yagi interpreted that the anomaly of the central peak results from that of heat capacity $C_X$. As mentioned before, their interpretation contains a problem, because $C_X$ is a scalar quantity and cannot show anisotropic anomaly. Finding out that the formula they used for $R_{LP}$ is valid only in isotropic materials, the authors generalize it for a solid and have an approximate expression:

$$R_{LP}\propto\frac{\alpha^2 T c_S}{\rho C_X}. \tag{2}$$

Here $\rho$ and $c_S$ are the density of sample and the elastic stiffness constant at constant entropy $S$, respectively. The temperature dependence and the anisotropy of $R_{LP}$ observed in Brillouin scattering can be explained very well by this equation; it is not $C_X$ but $\alpha^2$ that has the anisotropic nature and plays an important role in Eq. (2) as in the case of Eq. (1). From this successful explanation of the anisotropy of $R_{LP}$, it can be concluded that the physical origin of TGS is surely the thermal relaxational mode. Following this conclusion, the true spectral width of the central peak can be estimated from $1/\tau$ to be the order of 50–80 MHz in the case of 90° Brillouin scattering using a laser of wavelength 514.5 nm. This width is so narrow that the observable spectral width in Brillouin scattering would be restricted and determined only by the spectral resolution limit (about 1 GHz) of the Fabry-Pérot interferometer. No temperature dependence would be detected in the width. This is just the case seen in the Brillouin scatting experiment.[3]

Finally, the authors discuss the other interpretation about the physical origin of the central peak of TGS. Tokunaga proposed that the origin is a polarization relaxational mode.[4] The relaxation time of the polarization fluctuation has been determined by Brillouin scattering to be about $4\times10^{-11}$ sec at $T_c-T=1$ °C.[16] If the polarization relaxational mode is the origin, the spectral width of the central peak should be about 10 GHz. However, the observed width is around 1 GHz,[3] which indicates that the physical origin is not the polarization relaxational mode.

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