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ESR Study of SeO_2^- Radical in an Irradiated Single Crystal of Triglycine Selenate in the Vicinity of Phase Transition Temperature

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Detailed observations of the angular dependence of ESR spectra of SeO_2^- radicals formed by X-ray irradiation of a single crystal of ferroelectric triglycine selenate were carried out. Two kinds of SeO_2^- radicals were produced due to the difference in manner of selenium-oxygen bond scission. In spite of the difference in stability of radicals in TGSe and those in TGS, the behavior of SeO_2^- radicals in the phase transition region is in line with that expected from the result of X-ray diffraction study of TGS.

Various aspects of ferroelectric phase transition have been clarified by ESR technique with use of paramagnetic probes such as radiation damage and doped metal ions. As regards triglycine sulfate (TGS), X- or γ-ray irradiation has been effective for producing paramagnetic probes which are stable up to the transition temperature.[1—7] However, the stability of the resulting radicals in TGS and isomorphous triglycine selenate differs a great deal. In TGS, radicals from glycines II and III are stable while in TGSe those from acid ions are stable, indicating that the environments of radicals differ from each other. It is interesting to see whether the difference influences the behavior of radicals upon phase transition, resulting in a behavior differing from that expected from the result of X-ray diffraction study on TGS.

In view of the fact that the radicals are good probes for watching microscopic behavior of phase transition, the difference in the behavior of yielded radicals in isomorphous crystals might supply useful information.

In the mechanism of the phase transition in TGS, Hoshino *et al.*[8] postulated that acid ions change their structure and orientation at the phase transition point, and that they are located on the mirror planes at $b=1/4$ and 3/4 in the paraelectric phase. In isomorphous triglycine fluoberyllate (TGBe) the behavior of fluoberyllate ion has been studied by making use of ^{9}Be quadrupole perturbed NMR in deuterated crystals.[9] The results were in line with those of the X-ray diffraction study, the fluoberyllate ions being on the mirror planes at $b=1/4$ and 3/4 in the paraelectric phase.

No ESR study using paramagnetic probes has been reported for such behavior of acid ions mainly because of the lack of suitable probes.

The objective of this work is to clarify whether the stable radical produced from acid ions in TGSe reflects the general behavior of acid ions in TGS and its isomorphous crystals.

Experimental

Single crystals of TGSe were grown from aqueous solutions by slow cooling. After being irradiated by X-ray at room temperature for 1 h, the crystal was aged at room temperature for several weeks in order to reduce the unstable radicals produced from glycines.

The ESR spectrometer employed was operated at X-band, the second derivative signal being recorded. The position of the absorption line was determined by using DPPH as a standard. The temperature of the sample was controlled by a nitrogen gas stream and measured by a copper-constantan thermocouple attached to the crystal.

Results and Discussion

Stability of Radicals. In TGS two radical species are observed immediately after irradiation at room temperature.[3] They are assigned to $\dot{C}H_2COO^-$ produced from glycine I and $NH_3^+\dot{C}HCOO^-$ from glycines II and III. $\dot{C}H_2COO^-$ radicals have a half life of about one week at room temperature, while $NH_3^+\dot{C}HCOO^-$ is stable for a long period of time. In the case of TGSe, SeO_2^- radicals are formed from selenate ions in addition to radicals from glycines. The yield of the radicals from glycines is low, and they have a half life of several weeks. SeO_2^- radicals are quite stable, no decrease in signal intensity being observed. The difference in the stability of radicals formed from acid ions might be ascribed to the reactivity of the radical. However, the difference in the stability of the $NH_3^+\dot{C}HCOO^-$ radical indicates that the hydrogen-bonded network which stabilizes the radical is different. The radicals located in the network might give microscopic information on the difference in the surrounding which cannot be obtained from macroscopic properties such as Curie temperature and transition entropy.

Angular Dependence of SeO_2^- Radicals. The stable radical species produced in irradiated TGSe has been assigned to SeO_2^- radicals by Suzuki and Abe[10] by comparison of the principal values of hf-tensors of ^{77}Se with those of various oxy radicals of selenium. However, the structure and alignment of the radical has not been clarified in connection with the crystal structure.

The present results of angular dependence show that there are two major radicals which give eminent peaks in all of the three perpendicular planes. Figure 1 shows the observed angular dependence of the two species denoted by S1 and S2 in both the para- and ferroelectric phases. Weaker signals appear in certain directions.

The results of the tensor analysis with repect to a'bc orthogonal coordinate are given in Table 1, where a'⊥c lies in the ac plane. Both species S1 and S2 change the alignment upon phase transition. However, the principal values remain unchanged. Though there is a considerable discrepancy in the direction cosines, the principal values coincide with those of Suzuki and Abe.[10] In view of the difference in the angular dependence in

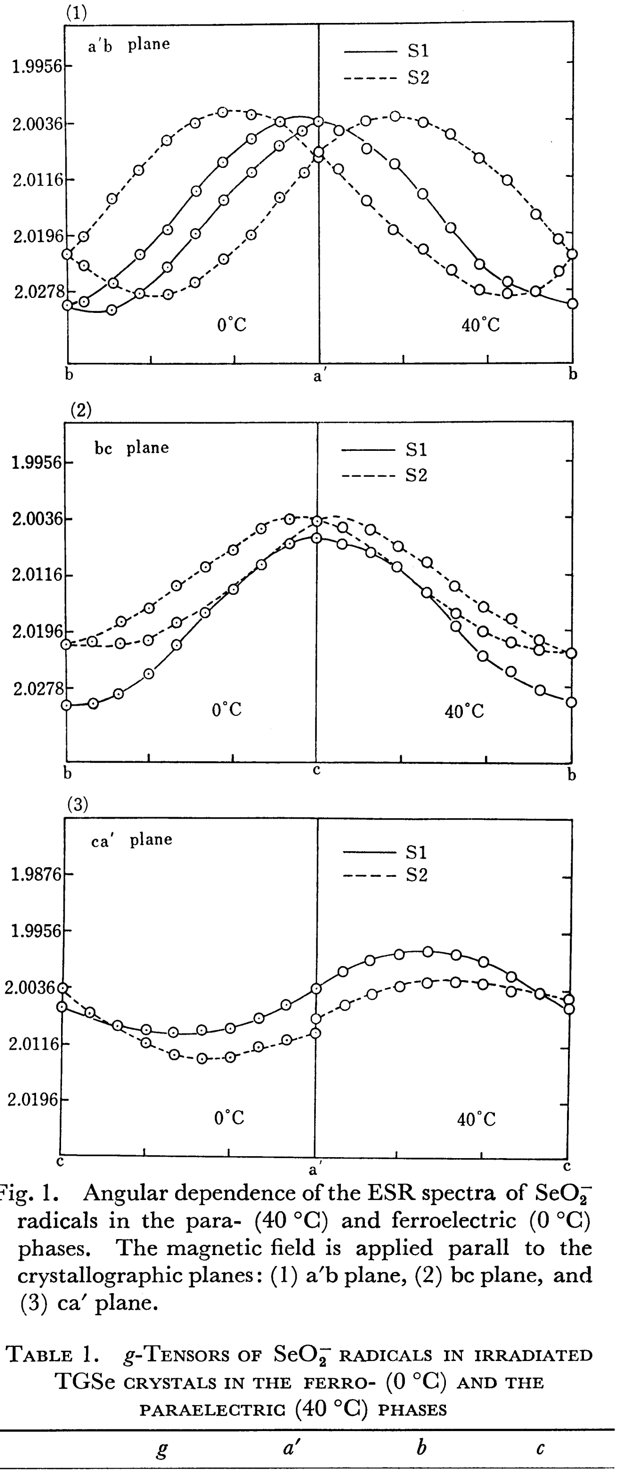

Fig. 1. Angular dependence of the ESR spectra of SeO_2^- radicals in the para- (40 °C) and ferroelectric (0 °C) phases. The magnetic field is applied parall to the crystallographic planes: (1) a′b plane, (2) bc plane, and (3) ca′ plane.

TABLE 1. *g*-TENSORS OF SeO_2^- RADICALS IN IRRADIATED TGSe CRYSTALS IN THE FERRO- (0 °C) AND THE PARAELECTRIC (40 °C) PHASES

	g	*a*′	*b*	*c*
S1 0 °C	2.028	0.067	±0.995	0.076
	2.009	−0.591	±0.022	0.803
	1.999	0.804	±0.096	0.586
S1 40 °C	2.027	0.0	1.0	0.0
	2.013	−0.585	0.0	0.811
	1.994	0.811	0.0	0.585
S2 0 °C	2.024	0.365	±0.898	0.246
	2.007	−0.573	±0.012	0.819
	2.000	0.733	±0.439	0.518
S2 40 °C	2.026	0.290	±0.829	0.470
	2.006	−0.600	±0.217	0.769
	2.001	0.739	±0.516	0.432

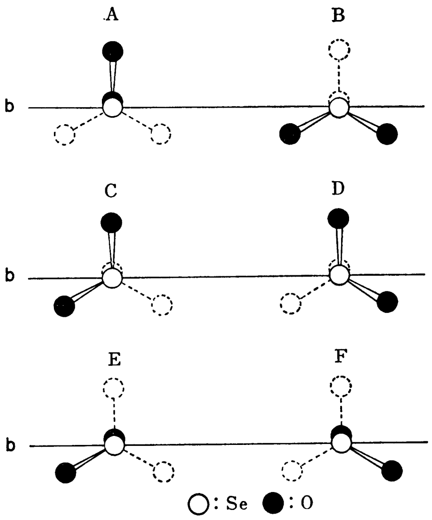

Fig. 2. Possible spatial configurations of SeO_2^- radicals produced from SeO_4^{2-} ion in TGSe crystals. The horizontal line shows the b-axis. S1 was assigned to B and S2 to E or F.

both the para- and ferroelectric phases, the most striking feature is that the site splitting of S1 in the ferroelectric phase disappears in the paraelectric phase.

There are six possible spatial configurations for SeO_2^- radicals in the paraelectric phase of TGSe crystals as shown in Fig. 2. Two of them (A, B) have mirror planes perpendicular to the b-axis. From the fact that the direction of the maximum principal value of the *g*-tensors in SeO_2^- corresponds to the direction combining two oxygen atoms[11,12] S1 is assigned to SeO_2^- of configuration B. The direction cosines of S2 have no such characteristics of S1 (Table 1) and are ascribed to configurations E and F in Fig. 2. The two configurations are crystallographically equivalent in the paraelectric phase. In the ferroelectric phase ESR spectra of configurations E and F should give a slightly different angular dependence caused by the different bond lengths of the two selenium-oxygen bonds, but this was not shown by experimental results.

The direction cosines of S1 and S2 show that S1 almost exactly keeps the configurations of the mother selenate ions even after the loss of two oxygen atoms. The direction cosines of SeO_2^- radicals calculated on the X-ray diffraction data for configurations B and F are given in Table 2. There is a considerable displacement of S2 from the site of the mother selenate ions as compar-

TABLE 2. CALCULATED DIRECTION COSINES FOR CONFIGURATIONS B AND F

Configuration		*a*′	*b*	*c*	Difference[a] (degree)
B	g_{max}	0	1	0	0
	g_{int}	−0.44	0	0.89	11
	g_{min}	0.89	0	0.44	11
F	g_{max}	0.39	±0.53	0.76	24
	g_{int}	−0.89	±0.44	0.15	41
	g_{min}	0.24	±0.72	0.63	34

[a] The angular deviation of the observed direction of S1 from B and that of S2 from F.

ed with the case of S1. This is reasonably explained by the fact that S1 has mirror symmetry but not S2. The selenate ions are stabilized by a network having a mirror symmetry because of the symmetry of the crystal. After the loss of two oxygen atoms S2 is forced to have asymmetric hydrogen bond system possibly causing displacement to seek a stable position.

Scission of Selenium-Oxygen Bonds. According to the crystal structure determined by X-ray diffraction[8] and neutron diffraction,[13] glycine I and one of the oxygen atoms in a sulfate ion are bonded by a short hydrogen bond (0.254 nm) in the TGS crystal. This is the shortest hydrogen bond connecting sulfate ion and neighboring glycines, the involved sulfur-oxygen bond having the longest bond length (0.148 nm) in a sulfate ion. In TGSe one of the lost oxygen in SeO_2^- corresponds to the oxygen atom with the longest sulfur-oxygen bond. The scission behavior of the selenate ion is in line with the fact that in a single crystal the breakage of the bond by irradiation tends to occur along the shortest hydrogen bond.[14]

Behavior of SeO_2^- *Radical upon Phase Transition.* As shown by the angular dependence of the *g*-value of the SeO_2^- radical, the orientations of radicals in the para- and ferroelectric phases differ. Particularly in the case of S1 disappearance of the site splitting was clearly observed in the a′b plane. In the bc plane the site splitting was too small as compared with linewidth even in the ferroelectric phase.

In the ferroelectric phase, the direction combining two oxygen atoms in SeO_2^- of configuration B has a finite angle with the b-axis, due to the lack of mirror symmetry. X-Ray diffraction study has shown that in TGS the sulfate ions do not have tetrahedral symmetry in the ferroelectric phase. In isomorphous TGSe, two selenium-oxygen bonds in SeO_2^- are thought to have a different bond length, causing the slightly different configurations of B in the ferroelectric phase. On the other hand, in the paraelectric phase the change of the structure makes the angle zero, resulting in mirror planes perpendicular to the b-axis. The result of tensor analysis shows the behavior to be consistent with that predicted by the result of X-ray diffraction study.[8] It should be noted that the behavior of radicals shows no influence expected from the difference in the stability of radicals. The magnitude of the site splitting gradually tends to zero without line broadening. It is hard to explain the absence of the line broadening in terms of the dynamic order-disorder mechanism.[15] It this system, the dynamic order-disorder mechanism assumes the interchange of two sites of S1 by thermal motion. When the interchange rate becomes greater, the site splitting should become smaller with exchange broadening.

The magnitude of the site splitting of S1 is not large enough as compared with the linewidth in the phase transition region. It was found that the alignment of S1 and S2 has a suitable relation for the observation of the change of the spectral feature in the critical region. In a certain direction, *i.e.* when the external field is slightly off from the b- and c-axis, each component of the signals from S1 and S2 completely collapses in the paraelectric phase because of the different temperature dependence of the alignment. The doublet splitting in this direction is sufficiently large in the ferroelectric phase to observe the temperature dependence. Figure 3 shows the difference between the resonance fields of the signals of S1 and S2 as a function of temperature. The plot shows that the change has a second order nature, the behavior of the radicals being in line with that of TGS.[16]

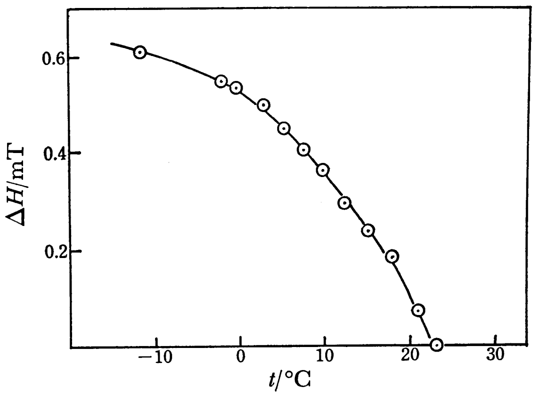

Fig. 3. Temperature dependence of the separation of ESR signals of S1 and S2. The magnetic field is applied slightly off from the b- and c-axis.

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