# ESR Study of squaric Acid

Ikuo SUZUKI

*Dept. of Engineering Science*

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Paramagnetic species produced by $\gamma$-rays in the crystal of $H_2SQ$ ($H_2C_4O_4$: 3, 4-dihydroxy-3 cyclobutene-1, 2-dione) were used to study the phase transition phenomena. The temperature dependence of the spectrum intensity was observed, whereas the spectrum had a constant linewidth and a constant hf coupling. The coupling proton is ordered at antiferroelectric phase.

## Introduction

Since the first synthesise of squaric acid, $H_2C_4O_4$ (3, 4-dihydroxy-3-cyclobutene-1, 2-dione) by Cohen et al in 1959[1], this material has attracted the attention of only chemists because of the peculiar structure of the molecule. Recently the crystal structure was determined by x-ray and neutron diffractions[2,3]. At room temperature the crystal system is monoclinic ($P2_1/m$) but pseudo body centered tetragonal (a=6. 13, b=5. 27, c=6. 14Å $\beta$=90. 00°). The $H_2C_4O_4$ molecule is planar and crystal consists of $C_4O_4$ groups linked by O-H···O hydrogen bonds to 4 neighbouring $C_4O_4$ groups in the layer. It was found that this material undergoes a second order antiferroelectric phase transition from a tetragonal to a monoclinic structure. A considerable isotope effect was found;

$T_{c,h}$=370K and $T_{c,d}$=516K, suggesting that the hydrogen bonds are essential in the mechanism of the phase transition[4].

Samuelsen et al suggested from partial birefringence and neutron scattering measurements that squaric acid is a two-dimensional ferroelectrics[5,6]. Raman and infrared spectra were measured by Baglin and Rose[7], and polarized Raman spectra have recently been measureed on single crystals by Nakashima and Balkanski[8].

It is an attractive subject to understand the phase change mechanism of this layer type crystal with magnetic resonance.

In this report we describe the preliminary study of the ESR spectra of irradiated squaric acid.

## Crystal Structure

Squaric acid is an unusually strong organic acid. The crystal structure at room temperature is monoclinic $P2_1/m$. the structure consists of planar layers of hydrogen-bonded molecules. In the high temperature phase the structure is believed to consist of planar four-fold $C_4O_4$ units with mean hydrogen atom positions at the centers of hydrogen bonds. The high temperature space group is the tetragonal I4/m. The molecules in one layer are related to the layers above and below by screw axes at $y$=1/4 and $y$=3/4, producing a pseudo-bodycentered tetragonal structure. (Fig. 1) In the low temperature phase only two hydrogens are close to any $C_4O_4$ unit. In Fig. 2 the vector sum of the hydrogen displacements is shown at each molecule[6]. This total displacement is expected to be proportional to the polarization of the unit, although the direction is not determined by symmetry and may be any direction in the $x$-$y$ plane. This axis should be determined by experimentally.

Thus the squaric acid consists of planar ferro= electric layers with the layers antiferroelectrically stacked. The wave vector associated with the phase transition is $q=\left(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right)$, i.e. the wavevector of the Z-point of the Brilliouin zone for the body=

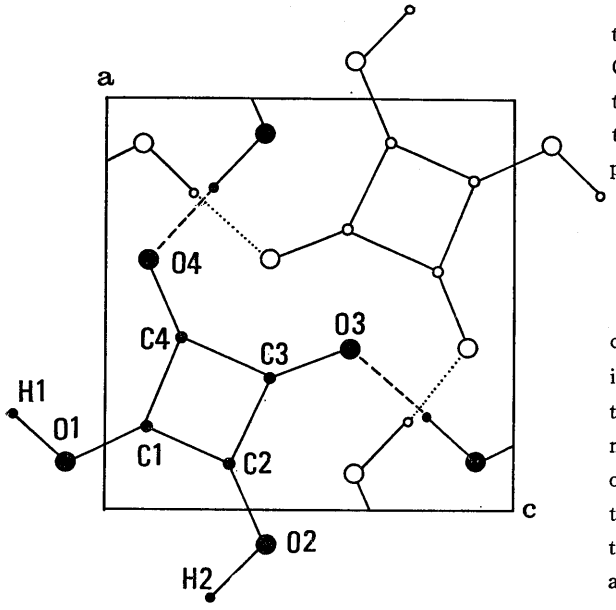



**Fig. 1** The structure of squaric acid at room temperature projected on the (010) plane. Two molecular layers are shown, at levels y=1/4 (open symbols) and y=3/4 (shaded symbols). The hydrogen bond are indicated by dashed lines [5].

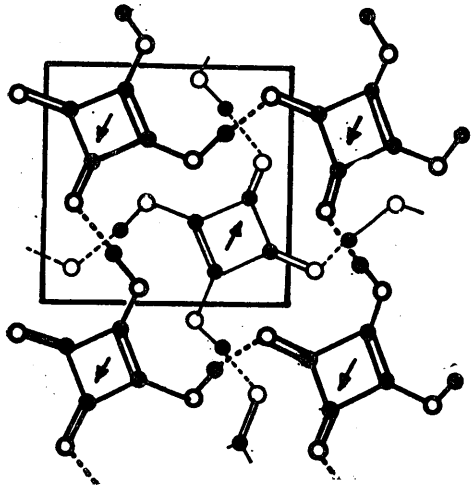


**Fig. 2** One layer of $H_2SQ$ with the vectors sum of the two hydrogen displacements indicated at the center of the $C_4O_4$ unit to which they belong [6].

centered tetragonal lattice,

The network of hydrogen bonds is similar to the antiferroelectric copper formate tetrahydrate $Cu(HCOO)_24H_2O$. Due to the extreme simplicity of the squaric acid crystal structure and the molecule, this material is the most ideal system for study of protonic "order-disorder" phase transitions.

## Experimental

This crystal has no paramagnetic ion. In the copper formate tetrahydrate, the ESR of of $Cu^{2+}$ ion is used for the probe of the phase transition. However the squaric acid has no such a paramagnetic ion, we must produce the paramagnetic centers by irradiation or dope the paramagnetic in order to study the phase transition by ESR. In this experiment, we irradiate the squaric acid with $Co^{60}$ $\gamma$-rays (about $2\times10^6$ rad.) at room temperature. For lower dosages we could not observe any resonance because of insufficient spin concentrations. Crystals irradiated at room temperature are brown in color. The paramagnetic centers are not stable at room temperature and the spectrum decays rapidly only in one day.

ESR mesurement was performed on the X-band spectrometer with 100 kHz field modulation in the temperature range from room temperature to 110°C and liquid nitrogen temperature, Fig. 3 shows the


**Fig. 3** ESR spectrum of $\gamma$-irradiated squaric acid ($H_2SQ$) at room temperature.

ESR spectrum at room temperature. In order to determine the number of paramagnetic centers, the saturation effects by microwave power were measured at room temperature. (Fig. 4) The saturation effects are very strong in these radicals. From the spectra we may consider that there are at

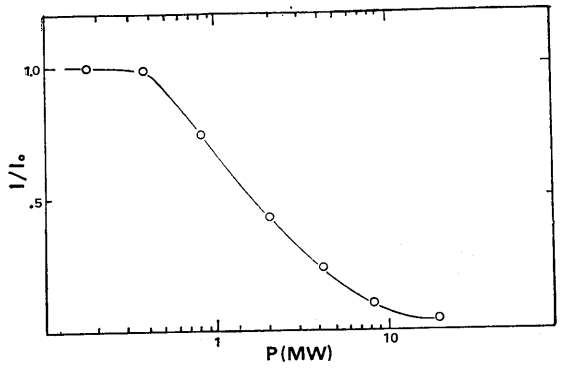



**Fig. 4** Saturation curves for the radicals at room temperatures.

least three kinds of protons which interact with the unpaired electron by *hf* coupling.

Figure 5 shows the ESR spectrum at liquid nitrogen temperature. In this temperature. we observed the same spectra. The central line splits from singlet to doublet by change of the crystal orientations.

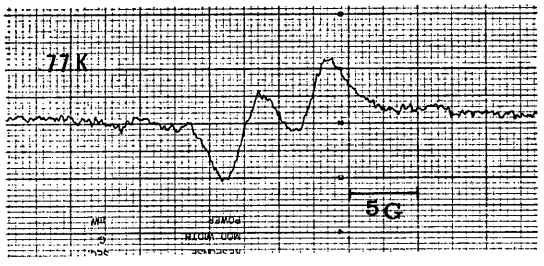


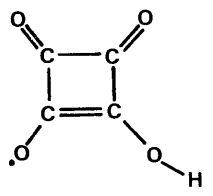

**Fig. 5** ESR spectrum of $\gamma$-irradiated squaric acid at liquid nitrogen temperature.

The line width of the central line has same values at both temperature (about 2.4 gauss). The *hfs* splitting is also constant. By this result we expect that the squaric acid has a $P2_1/m$ structure from the antiferrelectric phase transition point to liquid nitrogen temperature.

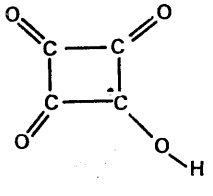
### Structure of the paramagnetic center

The distribution of unpaired electron of $\pi$-type radicals are estimated semiempirically for monocyclic radicals[9] Indeed some sort of linear relation between the unpaired-$\pi$-electron densities and the proton hyperfine splittings in $\pi$-type organic radicals is proposed. However, there is no report on the cyclobutadiene radical such as $H_2SQ$ organic crystal. In the following discussion we describe the central radical of the spectrum. This radical showed the considerable amount of anisotropy. The hyperfine anistotropy may be caused by dipolar interaction between unpaired electron and nuclear dipoles. In squaric acid it is protons which have a nuclear dipole moment. Because of the doublet spectrum, the paramagnetic center couples to only one proton in the molecules.

From these facts the following structures can be considered as the center in the irradiated squaric acid crystal.



(I)

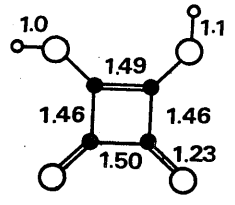


(II)

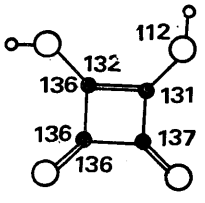
The dipolar interaction splitting is estimated by

$$H=\mu_e\mu_N\left\langle\frac{3\cos^2\theta-1}{r^3}\right\rangle$$

where $r$ represents the distance between an electron and a nucleus. $\mu_e$ and $\mu_N$ are, respectively, the electron and nuclear magnetic moments. Using the observed maximum splitting of 4.6 gauss, the distance was calculated as 2.63Å to radical (I). This distance is a little shorter than the determined value by neutron diffration (Fig. 6).




a




b

**Fig. 6** Schematical drawings of the molecule showing (a) bond length (Å), (b) angles (°) [4].

On considering the center (II) the hyperfine splittings of OH proton are usually less than 2.5 gauss as observed in HOĊHCOOH and ĊH₂O-H radicals. In the squaric acid the layer distance is very short, then the possibility that unpaired electron interacts

with next layers proton may be equally considerable. Indeedly the interlayer proton distance is shorter than intralayer proton. This facts is very important for the calculation of the second moment of NMR line[10]. In the copper formate tetrahydrate crystal, copper formate layer between the water layers has a very imporant role to the appearance of the antiferroelectricity of the crystal[11]. This interlayer interaction should be strong in the squaric acid.

Because the *hf* coupling constant is not function of the temperature, it seems to be ordered completely at room temperature.

Another paramagnetic centers have a little bit of isotropic coupling constants, like $\beta$-proton radicals. In this experiment the dimmension of sample was not sufficient to take spectra, in order to determine the *hf* coupling $A$ tensors. The precise determination of $A$ tensor is our next problem. And moreover we are planning to study of deuterated squaric acid crystals for precise identification of radicals. ENDOR experiments are desirable to determine the coupling protons.

### Temperature dependences of the ESR spectra

In the $KH_2PO_4$ crystal, which has a similar hydrogen network as a squaric acid crystal, protons are in ordered state. Two couplings protons were observed in irradiate $KH_2AsO_4$ crystals [12]. The similar two dimensional ordering of coupling protonis expected in squaric acid. To confirm this protonic ordering by resonance we observed the temperature dependence of the spectra. In KDP group, protons couples directly by to $PO_4^{3-}$ ion, these effects are observed clearly by *hfs* tensors of ESR spectra. However, we could not discuss in similar manner for the paramagnetic centers produced in irradiated squaric acid.

Observed spectra showed a temperature dependence (Fig. 7).

Since the ESR line shape is lorentzian, the peak-to-peak line width $\Delta H_{pp}$ is:

$$\Delta H_{pp}=\frac{1}{2\pi\sqrt{3}}\ \frac{1}{T_2}\left(\frac{h}{g\beta}\right)\text{(in gauss)}, \qquad (2)$$

where $T_2$ is the spin-spin relaxation time [13]. The temperature dependence of the line width was not observed, then the relaxation time $T_2$ is constant in this experimental temperature range. As the observed value of $\Delta H_{pp}$ is 2.4 gauss, the calculated value of $T_2$ is about $1.4\times10^{-8}$ sec. This value is typical value of solids.

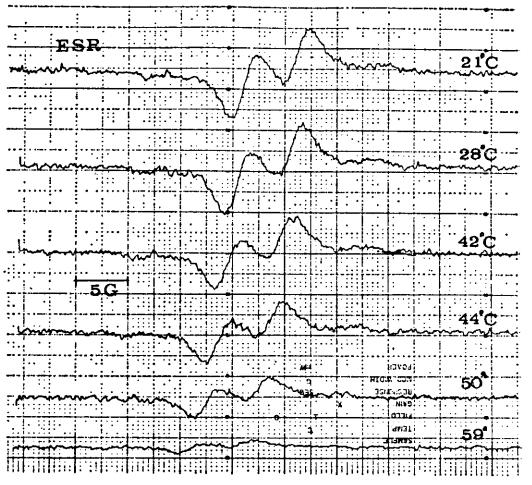



**Fig. 7** Temperature dependence of the resonance curves.

A simple way to estimate spin-lattice relaxation time $T_1$ of the paramagnetic center is performed by saturation method [13]. If the saturation factor $s$ is difined by

$$s=\frac{1}{1+\frac{1}{4}H_{1}^{2}\gamma^{2}T_1T_2} \qquad (3)$$

then the magnetic resonance absorption $Y$ and its first derivative $Y'$ have the forms

$$Y=\frac{sH_1y_m^0}{1+s(H-H_0)^2\gamma^2T_2^2} \qquad (4)$$

and

$$Y'=\frac{16(H-H_2)\gamma T_2s^2H_1y_m^{0\prime}}{3^{3/2}[1+s(H-H_0)^2\gamma^2T_2^2]^2} \qquad (5)$$

where $y_m$ and $y_m^0$ are the maximum amplitudes below saturation and $\gamma$ is the gyromagnetic ratio. The maximum of the peak-to-peak amplitude of the first derivative curve occurs when $s=2/3$, then at the maxima, the relaxation time is given

$$T_1=1.97\times10^{-7}\Delta H_{pp}/(gH_1^2) \qquad (6)$$

The microwave magnetic field $H_1$ at the sample may be computed from the microwave power P incident on the resonant cavity, and will have the functional dependence

$$H_1^2=K\cdot P \qquad (7)$$

In the irradiated center of $H_2SQ$, $H_{pp}=2.4$ gauss and

$H_1$=0.07 gauss, we obtain the relaxation time $T_1$ is about $5\times10^{-5}$ sec.

Below saturation the maximum amplitude $y'_m{}^0$ in eq. (5) is proportinal to the magnetic susceptibility $\chi''(\omega)$. The *rf* susceptibility $\chi''(\omega)$ is related to the static susceptibility $\chi_0$ by the Bloch equation. The static susceptibility $\chi_0$ is related to the *g* factor, spin *S*, and temperature *T* by the Curie-Weiss Law

$$\chi_0=\frac{Ng^2\beta^2S(S+1)}{3VkT} \qquad (8)$$

From this equation, we expect that the intensity of the average power obserbed per unit volume of the sample has a linear relation to $T^{-1}$ of the sample temperature. In Fig. 8 shows the distinct change of

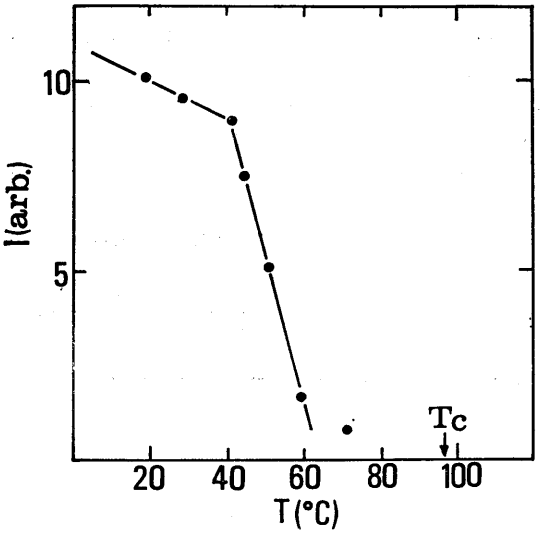



Fig. 8 Temperature dependence of the resonance intensity.

the absorption intensity above 40°C. Careful study of the temperature dependence of the neutron scattering intensities, Samuelsen and Semmingsen found the following realtion between intensities and temperature [5], which shows the two-dimensional character of squaric acid of phase transition,

$$I(hkl)=C(hkl)\times\varepsilon^{2\beta} \qquad (9)$$

The data were fitted between 65 and 96°C, where $\varepsilon=(T_c-T)/T_c$ (Fig. 9). The temperature variation of the neutron intensity, which is proportional to the order parameter; starts above 40°C.

Comparision with these data, the intensity decrease may be considered as some reflection of the order parameter. This order should have the effects

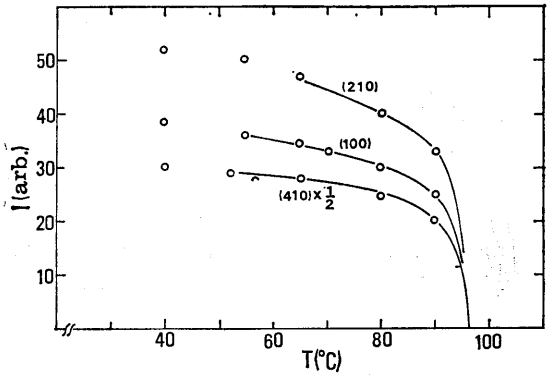



Fig. 9 Temperature variation of the neutron intensity [5].

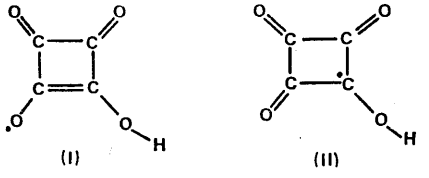
to the spin-lattice relaxation time. The experimental studies of relaxation time of irradiated organic acids were reported by many investigators [14),15)].

In this experiment, the ESR signals disappeared in the noise above 70°C. In order to reveal the relaxation mechanisms and the relations between the unpaired spin and the lattice phonons, we must use much sensitive ESR spectrometer.

These relaxation effects about proton spin will be reported in near future [10),16)].

## Conclusions

1) The following radicals are considered in irradiated squaric acid.




There is no reports such cyclobutadiene radicals.

2) The *hf* coupling protons are completly in order state below transition temperature. No temperature variation of *hf* splittings of the radical was obserrved to the transition point.

3) The spectral line width has a constant value in an antiferroelectric phase. The spin-spin relaxation time determined by the linewidth is about $1.4\times10^{-8}$ sec.

4) The temperature variation of the spectral intensity was observed above 40°C, as shown in neutron scattering measurements.
5) In liquid nitrogen temperature, the same paramagnetic centers are observed.

We confirmed that the coupling protons which have an important role of appearance of antiferroelectricity of this crystal is in order state below transition point. In next report we will analyse the dynamics of the proton, and the phase transition mechanism in the squaric acid by NMR experiments.

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