

Dielectric Dispersion of Triglycine Sulfate at Low Frequencies

By

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1. Introduction

Studies on the dielectric dispersion of triglycine sulfate at low frequencies have not been fully reported. Since it has been suggested that the ferroelectricity of the crystal of this compound may be due to the hydrogen bond like that of Rochelle salt, it was thought interesting to study the dielectric dispersion of the crystal at low frequencies, and to compare it with that of Rochelle salt which had been studied by the present authors.¹⁾ The result of the study has shown the similarity of the two substances.

2. Experimental Procedure

The dielectric measurement at frequencies between 1 kc/s and 1 c/s was done by the same apparatus described in a preceding paper.¹⁾²⁾

Single crystals of triglycine sulfate were prepared by the cooling and the evaporation methods, and (010) and (001) plates about 2mm in thickness cut from them were used in the measurement. The intensities of the low frequency field were kept as low as possible but could not be lowered below 2.5 V/cm. The relative humidity was kept at about 17% during the measurement.

3. Experimental Result and Discussion

(a) (010) plate

The experimental results obtained with (010) plates are as follows. The relation of the real part ϵ' and the imaginary part ϵ'' of the complex dielectric constant at several temperatures below the Curie point are shown in Fig. 1.

In the calculation of the value of ϵ'' correction was not made for the dc conductance error because they were negligibly small compared to the total conductance. From Fig. 1 there seem to be two dispersions as in Rochelle salt at temperatures below the Curie point.¹⁾ The result obtained with the same specimen as the above at temperatures above the Curie point is shown in Fig. 2, in which the existence of two dispersions is very easily seen.

Comparing Fig. 1 and Fig. 2 we find that the values of ϵ'' are generally larger

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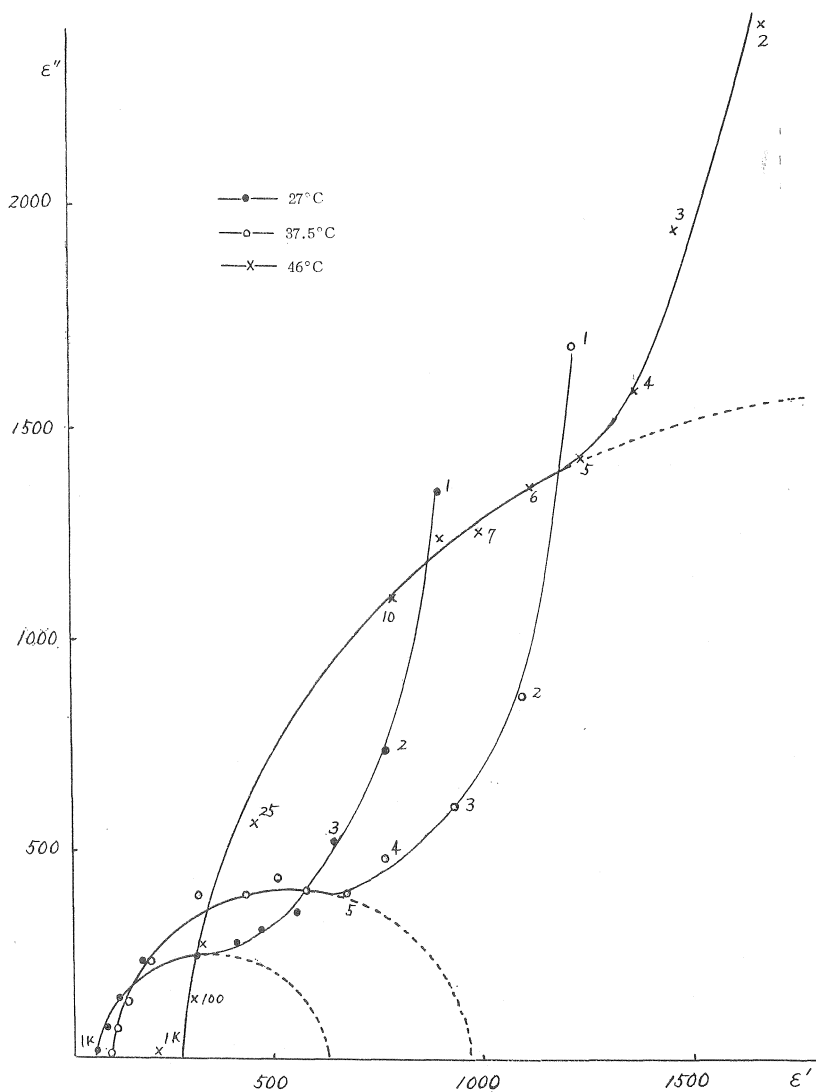


Fig. 1. Complex dielectric constants at several temperatures below the Curie point.

at temperatures below the Curie point than above it. This can not be attributed to the dc conductivity, which increases as the temperature rises. The difference of Fig. 1 and Fig. 2 can be explained in another way as follows. The second dispersion (dispersion at lower frequencies) occurs at frequencies of the order of a few c/s in every case. And this starting point is located on the left side of the top of the circular arc in the first dispersion at temperatures below the Curie point and on the right side at higher temperatures. This means that the relaxation time of first dispersion is much longer at temperatures below the Curie point than above.

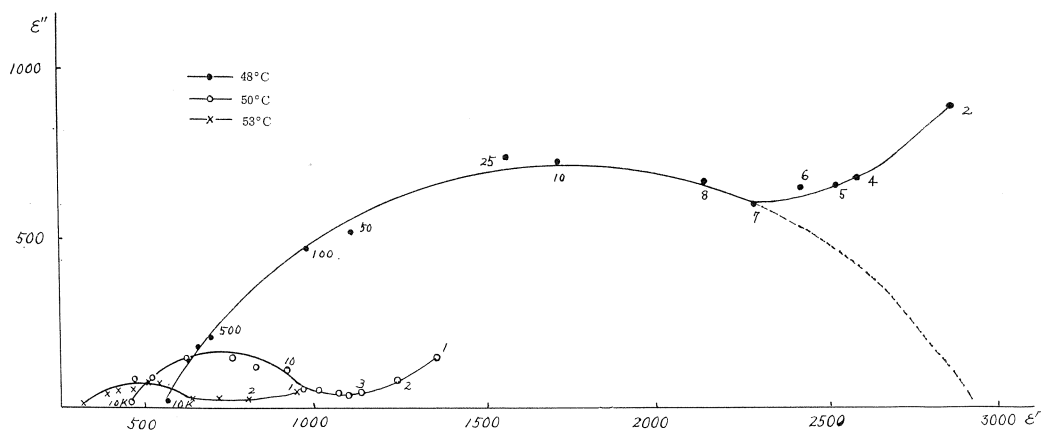


Fig. 2. Complex dielectric constants at several temperatures above the Curie point

The effect of poling

Fig. 3 shows the effect of poling. Curve (a) is the result with a virgin sample. Curve (b) is the result with the sample treated as follows. The virgin sample used in the measurement (a) was polarized in a dc field of 1.1 kV/cm for 3 minutes, and measured after the sample was aged for 30 minutes with the two electrodes short circuited. It is found that the values of ϵ' and ϵ'' decreased remarkably. When the sample was depolarized by heating it above the curie point the effect of the poling nearly disappeared.

Such effect was also found with Rochelle salt.¹⁾ Drougard and Young³⁾ have found that the dielectric constant of single crystals of barium titanate decreases as the average polarization decreases, and interpreted this fact as due to a domain clamping effect arising from the multidomain situation. So our result is contrary to theirs although the sample was not the same kind. On the other hand Furuhashi and Kurosaki⁴⁾ found similar effect to ours in regard to triglycine sulfate, and attributed it to the motion of domain wall as they observed variation of the effect by varying the intensity of the alternating electric field applied to

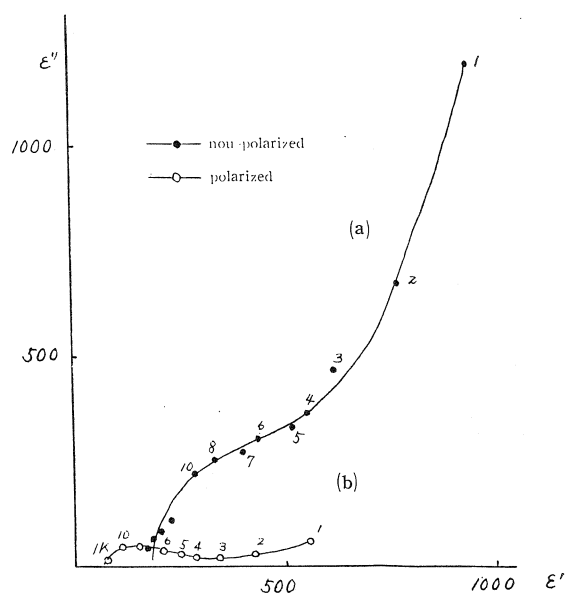


Fig. 3. The effect of poling (25°C)

the specimen for measurement. But we could not detect any conspicuous effect of the intensity of the field and supposed that the high dielectric constant of the non-polarized specimen was hardly due to the motion of domain wall. These supposition seems to be supported also by the fact that the dielectric dispersion of the sample above the Curie point is anomalous as below. Drougard and Young made the measurement at 20 kc/s, and Furuhata and Kurosaki at 100 c/s and we employed frequencies lower than these, so we examined the dependence of the effect of poling on frequencies. The result is shown in Fig. 4.

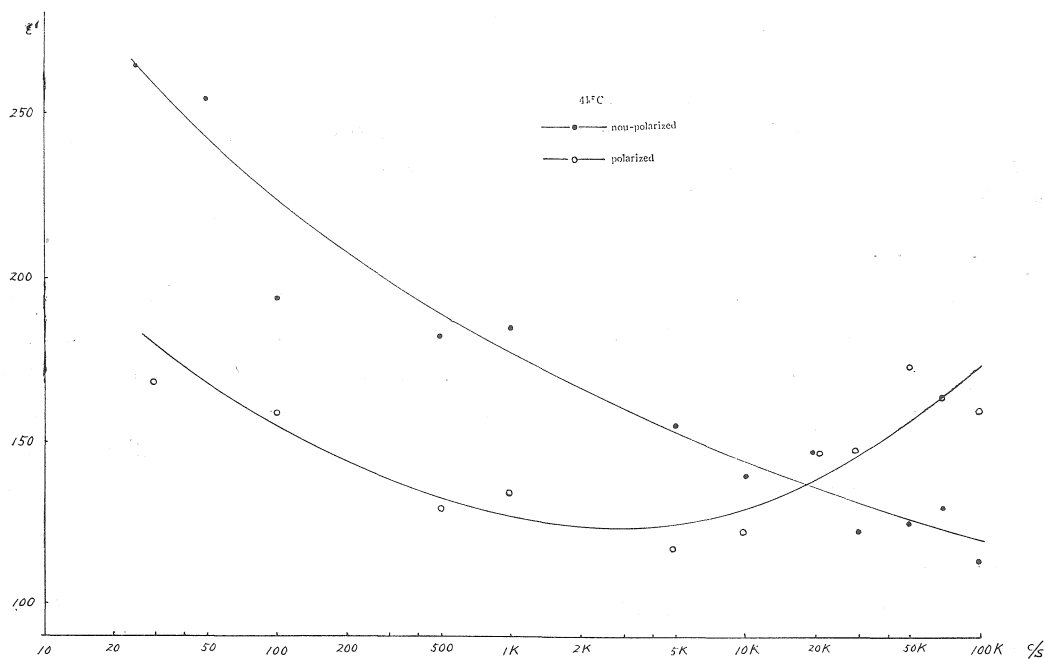


Fig. 4. The dependence of the effect of poling on frequencies (41°C)

It is found that the effect of poling reverses its sign at the frequency of about 10 kc/s and the value of ϵ' increases from 10 kc/s to 100 kc/s by poling. The latter fact will perhaps be attributed to the piezoelectric oscillation of the sample. And this oscillation seems not to be of the longitudinal but the bending type in view of the thickness (1.7mm) of the sample. After all the effect of poling seems to be decrease of ϵ' and ϵ'' . And this seems to be the characteristic feature of the ferroelectrics having hydrogen bond, but we must examine some other ferroelectrics to be sure about it.

The effect of X ray damage

The Cole-Cole diagram of the X ray damaged specimen, exposed for 6 hours to

40 kV 5mA X rays from a tungsten target at a distance of 10 cm, is shown in Fig. 5. When the X ray damaged crystals were heated above the Curie point and cooled again the effect of the X ray damage still remained.

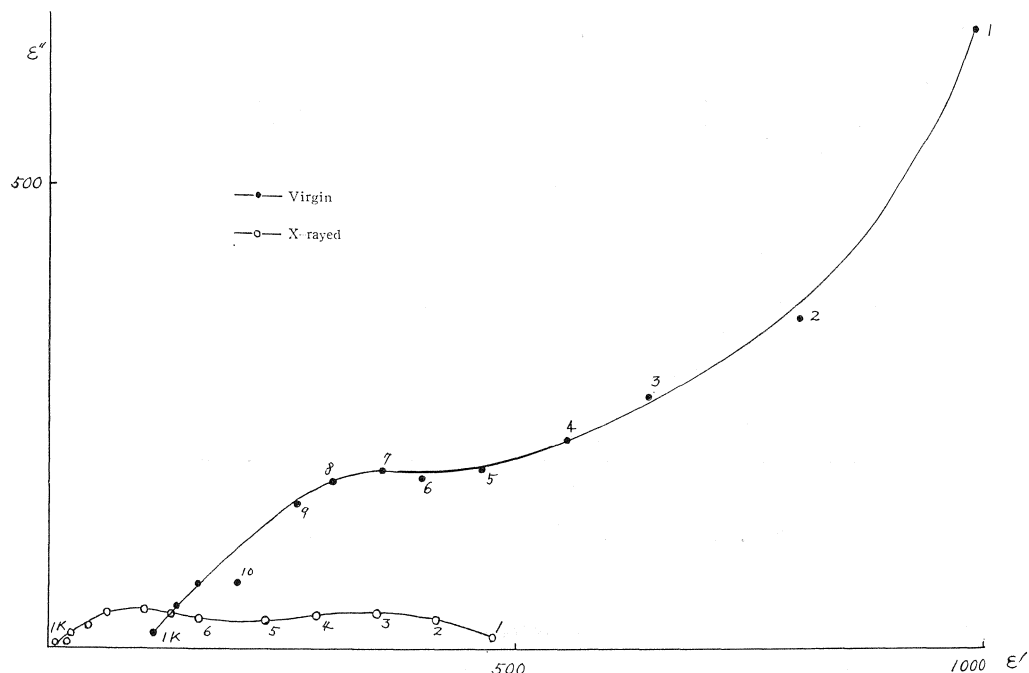


Fig. 5. Complex dielectric constants of X ray damaged sample (23°C)

Similar facts have been already found in Rochelle salts.¹⁾ Chynoweth⁵⁾ studied the hysteresis curve of X ray damaged triglycine sulfate and found the domain clamping effect of the radiation. He supposed that the effect of the radiation was to modify one minimum of the potential energy diagram not occupied by the ion. But to explain our experimental result we must presume the potential minimum occupied by the ion also suffers modification.

(b) (001) plate

In this case the values of ϵ'' were too small to be measured and so only the value of ϵ' were measured. The relations of ϵ' and frequency at several temperatures are shown in Fig. 6.

It is seen that the dielectric dispersion at low frequencies also exists in (001) plates. As the dispersion occurs at frequencies lower than a few c/s, it seems to be of the same kind as the second dispersion in (010) plates. Fig. 6 shows that this dispersion becomes smaller as the temperature rises. The effect of the dc electric field was not detected but some effect of X ray damage was noticed. We have not yet succeeded in thinking out a mechanism which will explain the facts about (010) and (001) plates.

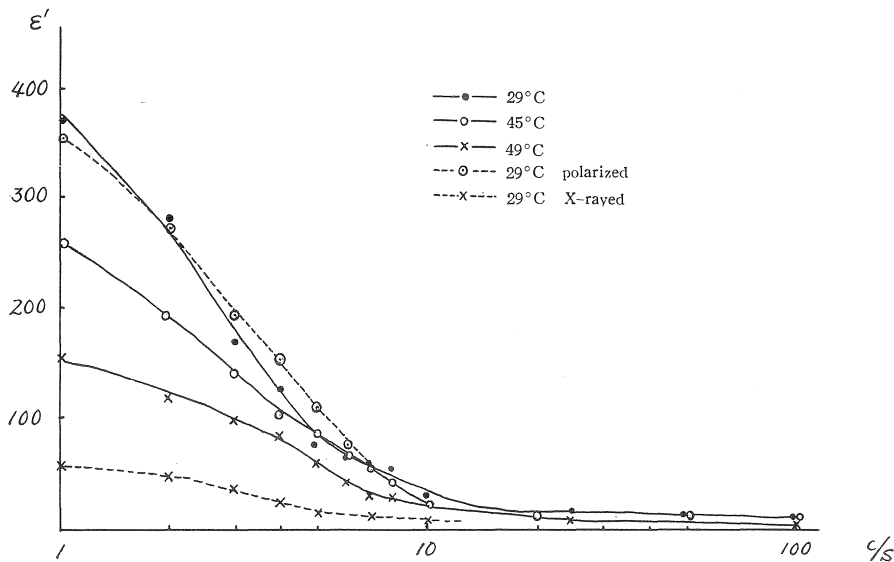


Fig. 6. The relations of ϵ' and frequency

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