

## MICROWAVE DIELECTRIC MEASUREMENTS OF GAMMA-IRRADIATED FERROELECTRIC AMMONIUM SULPHATE

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The behaviour of the complex dielectric constant of unirradiated and gamma-irradiated ferroelectric ammonium sulphate in the microwave region ( $X$  band) as a function of temperature is studied.

It is concluded that the ferroelectric transition point is shifted from  $-35^{\circ}\text{C}$  (for unirradiated samples) to  $-47^{\circ}\text{C}$  (for gamma-irradiated samples). Conclusions are reached regarding the thermodynamic aspects of the transformations and the modifications in the crystalline structure produced by gamma-irradiation.

### 1. Introduction

It is well known that ammonium sulphate undergoes a ferroelectric transition and that the dielectric constant is anomalous at this transition point.

In an earlier study [1], in which the complex dielectric constant was measured in the frequency range of 1–6 Mc/s (*cf.* [2,3]) or at microwave frequencies (*cf.* [4,5]), the transition point is defined at  $-50^{\circ}\text{C}$  or  $-36^{\circ}\text{C}$ . It is suggested [6] that it is possible to obtain different shapes of dielectric constant versus temperature curves for different frequencies [7] and irradiation [8, 9].

In our previous papers we have shown that paramagnetic defects are induced in gamma-irradiated ammonium sulphate [10–12]. In the present paper we study the behaviour of the temperature dependence of the complex dielectric constant of gamma-irradiated ferroelectric ammonium sulphate in the microwave region.

### 2. Experimental

For complex dielectric constant measurements we used a standard microwave installation (in  $X$  band). The installation's circuit and the calculation method used are described in a previous paper [13].

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The cavity was parallelepipedically shaped, with a  $TE_{102}$  mode ( $Q=3000$ ) and symmetric induction coupling hole, for low and high temperature measurements, as shown in Fig. 1.

Through the *S*-shaped spiral of copper flowed liquid nitrogen, the variable jet of which ensured slow modification of the cavity temperature. The rate of change of the temperature never exceeded the value of  $1^\circ\text{C}/\text{min}$ . Thermal insulation of the cavity from the rest of the installation was ensured by a teflon plate. A Cu-constantan thermocouple was used in temperature measurements. The thermocouple was placed at a point quite near the sample.

The parallelepipedically shaped sample was placed in one of the maxima of the *RF* electric field *E* of the cavity. The resonance frequency, quality factor of the cavity with and

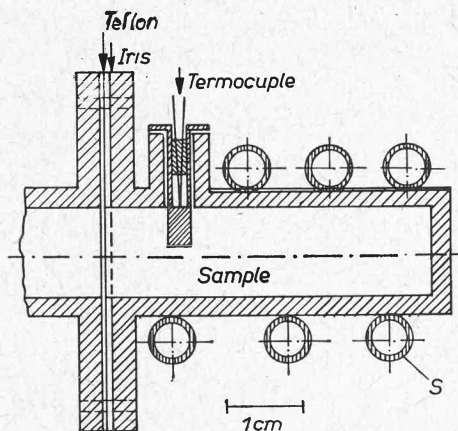


Fig. 1. Variable temperature cavity for dielectric measurements (from  $-100^\circ\text{C}$  to  $+200^\circ\text{C}$ )

without sample and the frequency shift at the introduction of the sample into the cavity were measured by means of a calibrated frequency meter with cavity of an accuracy of  $5 \times 10^{-6}$ .

Single crystals of ammonium sulphate were obtained by slow evaporation at room temperature from aqueous solution.

The irradiation of the sample was performed at room temperature by a  $^{60}\text{Co}$ -gamma source of activity  $3 \times 10^5$  rad/h.

### 3. Results and discussions

Unirradiated and irradiated single crystals, and also a crystal, treated thermally after irradiation, were used in the measurements.

For unirradiated samples, there is seen in Fig. 2*a* quick change of the  $\epsilon'$  and  $\epsilon''$  what indicates a transition from the paraelectric phase, at  $-36^\circ\text{C}$ .

For the gamma-irradiated samples, (Fig. 3) there is also an anomalous behaviour of  $\epsilon'$  and  $\epsilon''$  at a temperature of  $-47^\circ\text{C}$ .

In Fig. 3, a small anomaly can also be seen in the behaviour of the  $\epsilon'$  and  $\epsilon''$  at  $-36^\circ\text{C}$  point characteristic for unirradiated sample.

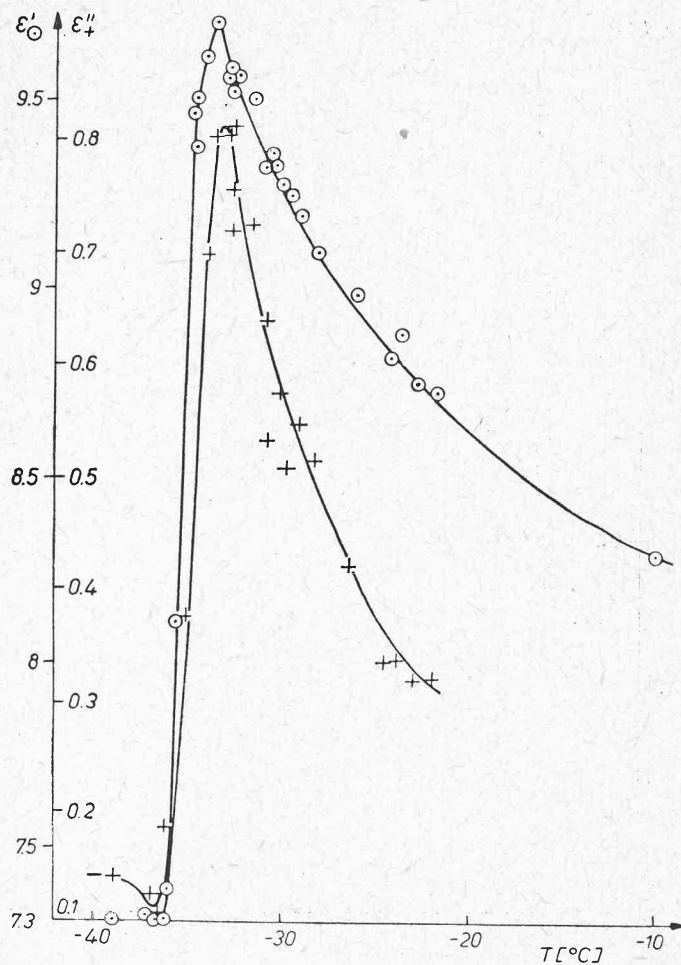


Fig. 2.  $\epsilon'$ ,  $\epsilon''$  vs  $T$  ( $^{\circ}\text{C}$ ) for unirradiated  $(\text{NH}_4)_2\text{SO}_4$

The transition point of the sample irradiated and thermally treated at  $+100^{\circ}\text{C}$  for one hour (Fig. 4) is similar to the ferroelectric point of transition of the unirradiated sample. A slight inflection of  $\epsilon'$  and  $\epsilon''$  in the vicinity of the temperature of  $-36^{\circ}\text{C}$  is also observed.

According to [9], as a result of the induced defects entropy in the Gibb's equation will change accordingly. We have at the transition point

$$H_1(T) + \delta H_1(T) = H_2(T) + \delta H_2(T) \quad (1)$$

(1-paraelectric phase, 2-ferroelectric phase), and

$$\Delta H = H_2 - H_1 = \Delta E - T\Delta S + p\Delta V$$

$$\delta H = \delta H_2 - \delta H_1 = \delta E - T\delta S + p\delta V \quad (2)$$

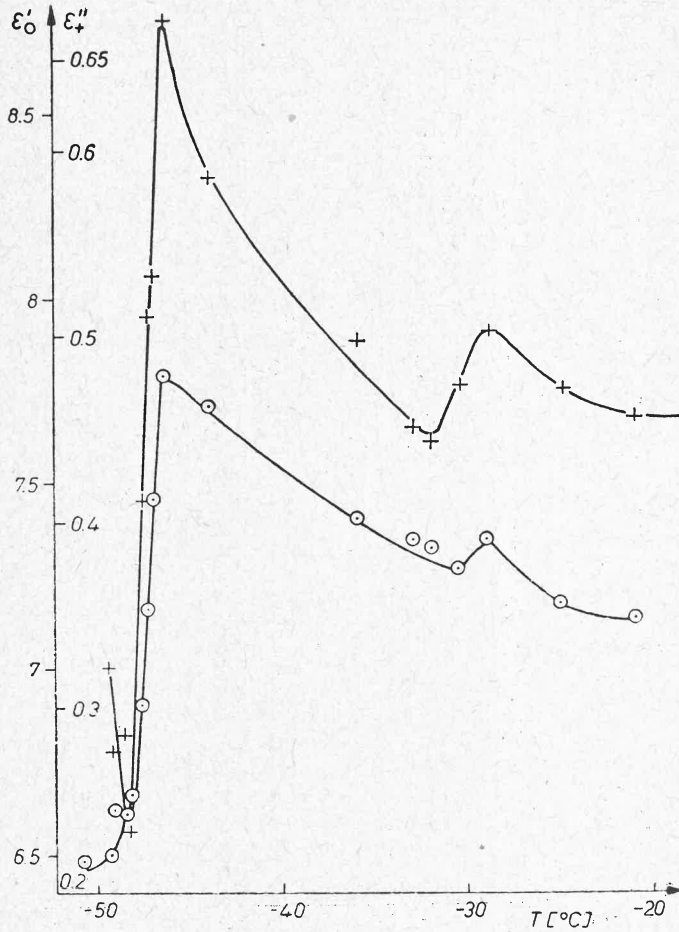


Fig. 3.  $\epsilon'$ ,  $\epsilon''$  vs  $T(^{\circ}\text{C})$  for gamma-irradiated  $(\text{NH}_4)_2\text{SO}_4$

Equation (1) becomes

$$\Delta H + \delta H = 0 \quad (3)$$

Because  $\delta H_2 \neq \delta H_1$ , the transition takes place at a temperature  $T \neq T_c$ .

In our case, as a result of the induced defects the transition takes place at a temperature lower than  $T_c$ ; this means that

$$\Delta H > 0$$

and

$$\delta H < 0 \quad (4)$$

Neglecting the volume term, sustenance of equation (4) necessitates

$$\delta E < 0, \delta S > 0$$

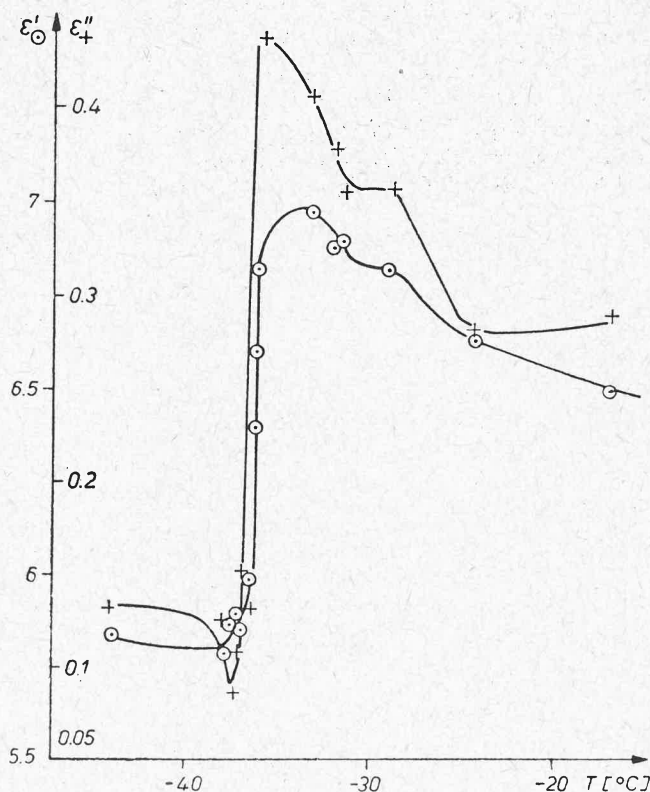


Fig. 4.  $\epsilon'$ ,  $\epsilon''$  vs  $T(^{\circ}\text{C})$  for  $(\text{NH}_4)_2\text{SO}_4$  gamma-irradiated and annealed at  $+100^{\circ}$

This means that the increase of the internal energy due to the defect will be smaller in the ferroelectric phase than in the paraelectric phase.

On the other hand, taking into account the nature of the ferroelectricity in ammonium sulphate [14], the irradiation produces modifications in the crystalline structure, what shift the transition point to a lower temperature.

The effect of annealing on the defects is a return of the lattice to its initial form and a shift of the transition point from  $-47^{\circ}\text{C}$  to  $-36^{\circ}\text{C}$  (Fig. 4).

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