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NMR investigations of triglycine-sulfate

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The ferroelectric behaviour of triglycine-sulfate (TGS; $[\text{CH}_2\text{NH}_2\text{COOH}]_3 \cdot \text{H}_2\text{SO}_4$) was first noticed in 1956 [1]. From optical and X-ray measurements this substance is known belonging to the monoclinic system. At room temperature the Laue symmetry is $2/m$; because of the ferroelectricity $P 2_1$ seems to be the most probable space group, but at temperatures higher than the Curie-point (47°C), the structure becomes more symmetrical, and the $P 2_1/m$ is the adequate space-group [2]. Another interesting observation was made by J. Stankowska and J. Stankowski [3]: « old » samples showed a two-fold hysteresis-loop, but after having subjected the sample to a heating process or to an a.c. field, the « rejuvenated » crystal showed the ordinary hysteresis-loop.

The aim of our nmr-investigations was to learn whether the H-atoms are responsible for the behaviour of the TGS. We observed the proton-resonance-line-shapes with the usual autodyne-spectrometer, using a magnetic field of about 3000 G.

From polycrystalline powder, we measured a second moment of

$$\overline{\Delta H_p^2} = 13,4 \text{ G}^2.$$

This value did not change in the range between 25°C and 60°C . The second moment of glycine-powder at room temperature was

$$\overline{\Delta H_p^2} = 16,5 \text{ G}^2.$$

The nmr-experiments of Kromhout and Moulton [4] tell us the glycine-molecules being not yet rigid at 25°C ; they assumed that at temperatures above -85°C , the amino-groups begin to rotate about the C-N bond; furthermore, they found the best agreement between the theoretical and the experimental values supposing a model, which may be written $\text{NH}_3^+ \cdot \text{CH}_2 \cdot \text{COO}^-$. The smaller second moment for TGS is caused

by the stretching of the lattice by the H_2SO_4 -molecules, leading to a weaker intermolecular coupling of the protons. Therefore it is probable the structure of the glycine-molecule in TGS being the same as proposed by Kromhout and Moulton. This result is in agreement with the conception, derived from dielectric measurements. The similar behaviour of ammonium-sulfate, guanidine-aluminium-sulfate a.o. concerning the spontaneous polarization is explained by an electrostatic interaction between the SO_4^{--} -ion and the other parts of the molecules; from these considerations, the formation of the NH_3^+ -group seems to be responsible for the ferroelectricity of TGS.

Further investigations were made with monocrystals*. We used two types: B, the b_0 -axis was always perpendicular to the magnetic field direction, and C, the c_0 -axis was always perpendicular to the magnetic field direction. In any case, the proton-spectra were observed in dependence on the angle between the b_0 - c_0 -plane and the direction of the field, Θ_B respectively Θ_C .

From the theory of spin-spin-interaction it follows that the line-shapes for Θ and $\Theta + 180^\circ$ must be always the same. In two-spin-systems or similar simple configurations of spins we furthermore expect the same proton-lines for the orientations $\pm \Theta$ or $90^\circ \pm \Theta$ whereby Θ may have any possible value. In more complicated systems consisting of different proton-groups, the last type of line-shape-symmetry depends on the space group, the crystal is belonging to. In our case, we did not observe such complete symmetrical behaviour neither for the B- or for the C-crystal. This result indicates that the TGS-crystal in the ferroelectric phase has no symmetry plane. But after heating up the crystals to about 60°C , only the C-crystal showed this symmetric change of line-shape. This proves the existence of a mirror plane at this temperature ($P 2_1/m$), which is perpendicular to the b_0 -axis. X-ray investigations [2] did not bring any change in crystal-structure when passing the Curie-point. Therefrom we see that the ferroelectric phase is only due to the configuration of the H-atoms.

This change in line-shape on both sides of the Curie-point depends strongly on the orientation of the crystal in the magnetic field. It is of utmost importance to get out from this angular dependence the respective

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proton groups, which are responsible for this transition. But for this it would be necessary to know more details of the situations of the N-, C- and O-atoms in the elementary cell. Hitherto only vague suppositions are possible.

At last, we have to mention, that a rejuvenescence process was not detected with surety.

The experimental part of this investigation was done by Miss D. Dietze and I am very grateful for her help.

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