

Zeitschrift: Archives des sciences [1948-1980]
Herausgeber: Société de Physique et d'Histoire Naturelle de Genève
Band: 13 (1960)
Heft: 9: Colloque Ampère

Artikel: NMR investigations of triglycine-sulfate
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DOI: <https://doi.org/10.5169/seals-738604>

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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^{2-} -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

* We are grateful to Dr. R. Nitsche, Zürich, for his advices concerning the production of monocrystals, and to Dr. J. Stankowski for sending us some specimen for control.

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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