# Glassy Crystals VI.
# Nitrogen-14 Quadrupole Resonance in Glassy Crystalline Thiazole*

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Crystalline thiazole has been studied by nitrogen-14 nuclear quadrupole resonance in the 77–206 K temperature interval that contains a glass transition at 174 K. The temperature dependences of the relaxation time $T_1$, of the frequencies and the amplitudes of the NQR signals have been determined for lines $\nu_+$ and $\nu_-$. No crystal-crystal phase transition has been observed, so that the glass transition at $T_g'$ can be observed on heating and on cooling. The $T_1$ measurements have shown the existence of a large-amplitude motion which is different from that which is "frozen" at $T_g'$: it corresponds to a secondary relaxation process which is still active in the glassy crystalline phase. Further studies will attempt to assign it to a definite molecular motion.

## I. Introduction

Some dynamically disordered crystalline phases can be quenched at low temperature to yield what Seki and coworkers [1] called "glassy crystals". A glassy crystal is a crystal from the crystallographer's point of view. It is also a glass according to thermodynamic criteria: it exhibits an enthalpic relaxation, a glass transition can be observed on heating, by means of calorimetric measurements, and a residual entropy at $T \rightarrow 0$ can generally be determined [2]. It can be considered that glassy crystals are good models for the glassy state and their study should lead to a valid description of general structural and dynamic properties of glasses [3].

In ordinary molecular glasses both positional and orientational disorders are shown to exist by means of X-ray measurements. On the contrary, in the two glassy crystals thoroughly described so far, cyclohexanol [4] and 1-cyanoadamantane [5], single crystal X-ray studies have shown that the time and space averaged structure is retained in the quenching process from the dynamically disordered state to the glassy crystalline one. Therefore, in the glassy crystalline state, the positional crystalline lattice is retained and disorder arises from the different orientational positions that each molecule can attain. This represents an important simplification with respect to ordinary glasses.

In ordinary glasses, nuclear quadrupole levels are so broadened by the spread of the intermolecular contribution to the electric field gradient tensor that the intensities of NQR signals is tremendously reduced and the signals fall beyond the detection sensitivity of standard NQR techniques. In glassy crystals, as said above, the molecules are regularly located at the nodes of a periodical crystal lattice though they are randomly distributed among a definite number of discrete possible orientations. The disorder is not as important as the general disorder of ordinary glasses and it is possible to observe the nitrogen-14 NQR lines in glassy crystalline 1-cyanoadamantane. This was helpful to establish that the occurrence of the glass transition on cooling is related to the "freezing" of the tumbling motion of the molecule in the solid phase, while reorientation around the threefold molecular axis continues in the glassy phase [6].

Such a dynamic behaviour has been observed in other cases [7, 8], and it can be thought that glass transitions are to be systematically assigned to the freezing of some large-amplitude molecular motion provided some symmetry conditions are fulfilled [7]. To get a more thorough understanding of the glass transition mechanism, we looked for better model glassy crystals. We thought it necessary to get solids in which no crystallization towards a more stable

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crystalline phase would occur (as in cyclohexanol and 1-cyanoadamantane) so that the glass transition could be studied from both the "hot" and the "cold" sides. A rigid molecule made of a few atoms would prevent the interference of intramolecular conversion motions (as in cyclohexanol) and eventually allow molecular dynamics computer simulations to be performed. Such a molecule would presumably give rise to simple large-amplitude motions, hopefully to a single one. A series of thermodynamic, dynamic and structural experiments led to the discovery of a glassy crystalline phase in each of the two crystalline phase sequences of thiophene [9]. Every one of the above mentioned conditions seems to be fulfilled; unfortunately, the low values of the glass transition temperatures (~ 40 K) make the experimental investigations difficult. Three other five-membered heterocyclic compounds were studied and were shown to yield glassy crystalline phases with glass transitions in the 130 – 170 K temperature range [10]. In particular, thiazole had been previously studied by Goursot and Westrum [11] who have observed a glass-like transition, $T'_g$, between 145 and 175 K by means of calorimetric measurements. Our differential scanning calorimetry (DSC) experiments show that the value of the heat capacity increment at $T'_g$ depends on thermal treatment, so that $T'_g$ is a glass transition indeed [10]. No other phase transition and no unwanted crystallization has ever been observed in purified thiazole.

The present work is a first study of the large-amplitude motions in crystalline thiazole on both sides of the glass transition temperature.

## II. Experimental

*a) Material.* Thiazole purchased from Janssen Chimica was purified by distillation through a spinning band column; about 25 g were sealed under vacuum in a glass vial. The purity was found to be 99.4 mole percent by gas chromatography on a capillary SF54 column with helium as carrier gas. Another sample of thiazole, sealed under atmospheric pressure without any purification about 10 years ago, was also used for preliminary measurements. It is of a brownish colour likely due to impurities or oxidation compounds which were not analyzed. In what follows the sample used is the purified one unless it is specified as the "unpurified thiazole sample".

b) Instrumentation and measurements. The NQR spectrometer is a laboratory built automated pulsed system with signal accumulation and processing [12]. In the thiazole samples studied the nitrogen-14 NQR FID signals are short enough to mainly occur during the recovery time of the receiver and attention was then focussed on the echo signal following a 90 – 180° pulse sequence. The relaxation time was determined at different temperatures (Fig. 1) by studying the amplitude of the echo signal as a function of the time elapsed after the sample was saturated by a series of closely spaced 90° pulses and before the 90 – 180° sequence is applied. As a side product of this investigation, it has been possible to obtain the temperature dependence of the NQR frequencies $\nu_+$ and $\nu_-$ (Fig. 2) and the amplitude of the NQR signals (Figure 3). Depending upon the actual S/N ratio at a given temperature for one of the $\nu_+$ and $\nu_-$ lines in a given sample, accumulation from 64 to 1024 signals was made. For the determination of the maximum amplitude $A_0$ of the signal, the sample was allowed to relax during a time four or five times $T_1$ ($T_1$ varies between 1.5 and 35 s for $\nu_+$ and $\nu_-$ lines in the temperature range studied).

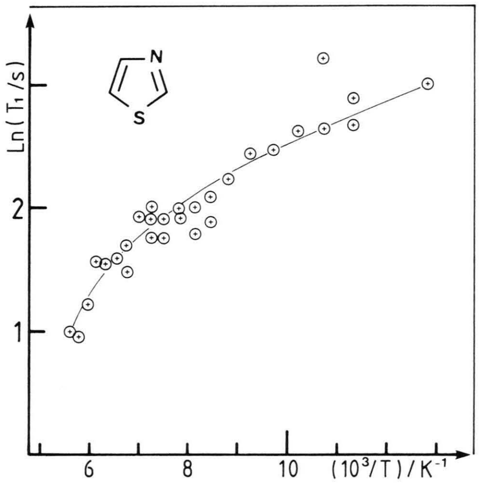

Fig. 1. Temperature dependence of the relaxation time $T_1$ of the $\nu_+$ nitrogen-14 NQR line in crystalline thiazole. The solid line corresponds to the fitted relationship

$$\frac{1}{T_1} = 8.17 \times 10^{-6}\, T^2 + 3.24 \times 10^4 \exp\left\{-\frac{2250}{T}\right\}.$$

The curve for $\nu_-$, not shown, is similar.

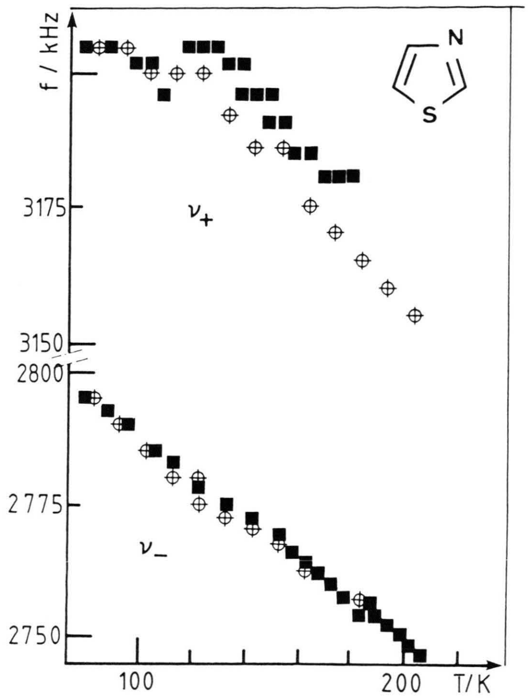

Fig. 2. Temperature dependence of the frequency of the $\nu_+$ and $\nu_-$ nitrogen-14 NQR lines in crystalline thiazole as obtained with the purified (■) and unpurified (⊕) samples. The small signal to noise ratio and the line width (~ 3 kHz) make the accuracy of the frequency determination poor and explain the dispersion of the experimental points. The increase of about 5 kHz in $\nu_+$ between the unpurified and purified samples is still unexplained.

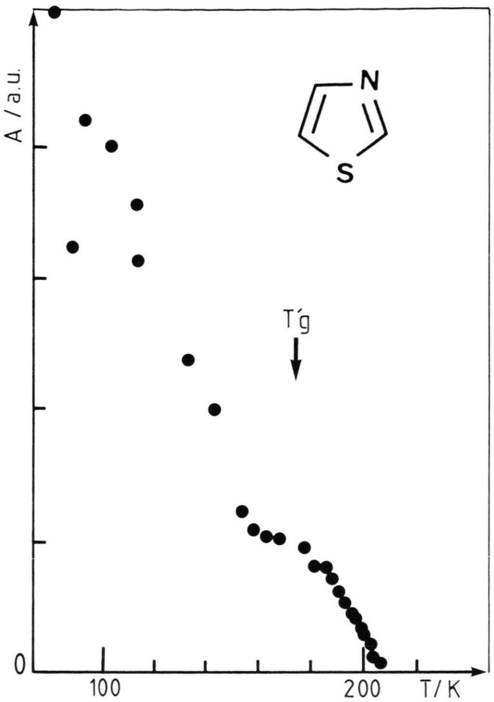

Fig. 3. Temperature dependence of the amplitude of the $\nu_-$ nitrogen-14 NQR signal in crystalline thiazole. Below 180 K, the measurements were made with increasing temperature only; above 180 K, they were made both with increasing and decreasing temperature.

## III. Results and Discussion

At 77 K, two nitrogen-14 NQR signals corresponding to the $\nu_+$ and $\nu_-$ transitions were recorded at 3.205 and 2.795 MHz, respectively. These values are quite different from those reported by Redshaw et al. [13], i.e. 3.379 and 2.902 MHz. The frequency ranges around the frequencies reported by Redshaw et al. were carefully searched and the sample submitted to several thermal treatments including fast cooling of the sample by immersing it in liquid nitrogen, slow cooling over a period of one hour inside a thick copper box, and thermal annealing by heating to the glass-like transition temperature: no line other than those we first observed could be detected.

As DSC measurements performed on a sample of impure thiazole (different in origin from that of the unpurified sample prepared for NQR study but of similar brownish colour) revealed a phase transition near 220 K and no other one, it was hoped that such a phase transition would also appear in the NQR unpurified sample leading to a low temperature phase which would reveal Redshaw et al.'s NQR signal frequencies. Therefore, another search was made with the NQR unpurified sample but again no signal was observed except the first ones reported above.

As DSC measurements performed on a sample of pure thiazole reveal a behaviour similar to that reported by Goursot and Westrum [11], it is concluded that the lines we have observed in both NQR samples correspond to the phase exhibiting a glass transition near 170 K.

Redshaw et al.'s frequencies should belong to another crystalline phase we were unable to obtain.

The quadrupole coupling constant, $e^2Qq/h$, and asymmetry parameter, $\eta$, corresponding to the lines observed at 77 K, are

$$e^2 Q q/h = \tfrac{2}{3}(\nu_+ + \nu_-) = 4.000 \text{ MHz},$$

$$\eta = 3(\nu_+ - \nu_-)/(\nu_+ + \nu_-) = 0.21 .$$

Though the temperature dependence of the nitrogen-14 NQR frequencies in thiazole is presented as a side-product of the relaxation time study, we shall consider it first. As stated in the figure caption, the weakness of the recorded signals, even after accumulation, explains the lack of accuracy in the positions of the experimental points against the frequency scale. The intensity of the $\nu_-$ line is larger by a factor of two than that of the $\nu_+$ one, an unusual feature because it is usually the other way around. As a result, experimental points for the $\nu_-$ line are more regularly disposed in the figure and from the smoothness of the curve which may be drawn through these points it appears that a crystal-crystal phase transition is utterly improbable in the studied temperature range. No accident is seen near $T'_g$ and none was expected because of the usual structural continuity between a glassy state and its mother phase.

On heating, the amplitudes of the NQR signals decrease until they become unobservable near 206 K (Figure 3). This decrease is more rapid that it would be in an usual rigid crystal: for instance, at 200 K, the $\nu_-$ signal is seven times weaker than that which would be expected from Boltzmann law. Such amplitude decreases have already been observed in solids within which large-amplitude motions are activated when temperature increases, for example in hydrazine [14]. They are usually accompanied by modifications of the signal widths which reveal the fact that the solid is no longer "rigid" from the NQR point of view (correlation times of the order of $10^{-4}$ s). But in the case of thiazole, the echo width at half-height remains constant, $92 \pm 12$ µs, from 77 to 206 K. This corresponds approximately to a 3 kHz line width, which is large as compared to line widths observed in ordered crystals. In glassy crystalline 1-cyanoadamantane, the line width had the same value, $\sim 3$ kHz, whereas it was only $\sim 0.2$ kHz in rigid ordered phase II (reference 6 gives 10 kHz and 0.5 kHz for the two phases, respectively, but a $\pi^{-1}$ factor had been omitted). Again, large NQR line widths are observed in a glassy crystalline phase, which obviously are to be related to static disorder.

It is to be noticed that, in unpurified thiazole, the line width is only half as large as in purified one, that is 1.5 kHz. This could indicate that there is less disorder in the impure solid compound, which is rather surprising.

A noticeable inflexion can be seen between 160 and 175 K on the curve which represents the temperature dependence of the amplitude of the $\nu_-$ echo (Figure 3). Such an inflexion has also been observed on the corresponding curve for the $\nu_+$ line which was measured during another experimental run. A further experimental study of this phenomenon, which occurs near $T'_g$, together with $T_2$ measurements, will be undertaken in the near future to make sure that it is not an artefact and eventually to understand its relationship to the glass transition mechanism.

Relaxation time $T_1$ has been measured from 77 to 178 K. The results are almost identical for both thiazole samples. Figure 1 shows the temperature dependence of $\ln T_1$ as determined for the $\nu_+$ line. It can be fairly represented through the fitted expression

$$\frac{1}{T_1} = 8.17 \times 10^{-6}\, T^2 + 3.24 \times 10^4 \exp(-2250/T) . \quad (1)$$

A similar expression is found for $\ln T_1$ for the $\nu_-$ line. The coefficients of the first and second terms are $3.59 \times 10^{-6}$ and $3.39 \times 10^4$, respectively.

The term depending on $T^2$ is supposed to represent the influence of librations on $T_1$ [15] and it dominates at low temperatures. The second term represents the influence of some large-amplitude reorientational molecular motion with an activation enthalpy of 18.7 kJ · mol$^{-1}$. It contributes to $T_1$ for only 2 percent at 140 K but becomes predominant around 190 K.

According to DSC measurements, the glass transition temperature is equal to 174 K for a heating rate of $\sim 0.2$ K · s$^{-1}$. This corresponds to a correlation time of $\sim 150$ s$^{(3)}$ (or about $10^{-3}$ Hz) for the motion the freezing of which is correlated with $T'_g$. It is highly improbable that a motion with a frequency of $10^{-3}$ Hz (or lower at lower temperatures) could influence $T_1$ even with a 2 percent contribution at 140 K. Therefore, the large-amplitude molecular motion acting on $T_1$ is not the motion that is "frozen" at $T'_g$. It is some other molecular motion which still exists in the glassy crystalline phase, that is what is generally called a secondary (or $\beta$) relaxation process. The value of the measured activation enthalpy corresponds to what is expected for a $\beta$ process [16].

Now, we are facing a set of contradictory data. We have seen that the NQR signals disappear at 206 K with the same line widths as at 77 K and with amplitudes that decrease more rapidly than Boltzmann law would explain. Furthermore, the $T_1$ value at 206 K, as calculated from formula 1, is still large, about 1 s. This does not support the model of signal disappearance through the emergence of some rapid reorientational motion. The reasons for this behaviour are not yet clear, but it should be admitted that the frequency of the $\beta$ motion at 206 K is noticeably lower than the NQR line width, that is $3 \times 10^3$ Hz. So, the frequencies of the $\beta$ motion comply to

$$f \ll 3 \times 10^3 \exp\left\{-2250\left(\frac{1}{T} - \frac{1}{206}\right)\right\}. \qquad (2)$$

Moreover, crystalline thiazole near its melting temperature, 239 K, exhibits the same glassy aspect as any plastic crystal does. From our experience, such an aspect for a polycrystalline sample near melting is characteristic of very fast reorientational molecular motions ($10^6$ Hz or faster). But extrapolating from (2), the frequency of the $\beta$ motion at melting would be

$$f_\beta^{239\,\mathrm{K}} \ll 1.4 \times 10^4\ \mathrm{Hz}$$

which is much lower than expected.

## IV. Conclusions

This study of glassy crystalline thiazole is meant as a preliminary investigation of the dynamics of the large-amplitude molecular motions within the solid. It has shown that no crystal-crystal phase transition exists between 77 and 206 K. This confirms that thiazole is a good experimental model system in which no unwanted crystallization will hinder the study of the glass transition on heating and on cooling.

Relaxation time measurements has disclosed the existence of a large-amplitude motion which is not the motion the freezing of which is correlated with the glass transition at 174 K. It corresponds to a secondary relaxation process which will have to be assigned to a given molecular motion. A further NQR work, in particular on the temperature dependences of the NQR signal amplitudes and of relaxation time $T_2$, should be helpful. Together with this NQR study, dielectric measurements will take advantage of the large dipole moment of the thiazole molecule, 1.6 Debye, to get the dynamic characteristics of this $\beta$ relaxation.

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