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An NQR study of the thermally activated motion of nitro groups in 3-nitrobenzene sulphonyl chloride

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Abstract. A study of the temperature dependence of the ^{35}Cl NQR frequency and linewidth, and the ^{35}Cl and ^{37}Cl spin–lattice relaxation times, in 3-nitrobenzene sulphonyl chloride (3: NO_2 - ϕ - SO_2Cl) is reported. The pressure dependence of the ^{35}Cl frequency is also reported. The latter measurements indicate the existence of a first-order phase transition induced by pressure. It is shown that all the results are consistent with the onset of reorientations of NO_2 groups. The parameters deduced, including the activation energy, are compared with those obtained from previous studies of 2: NO_2 - ϕ - SO_2Cl and 4: NO_2 - ϕ - SO_2Cl .

1. Introduction

In previous papers [1,2] comprehensive studies of 2-nitrobenzene sulphonyl chloride (2: NO_2 - ϕ - SO_2Cl) and 4-nitrobenzene sulphonyl chloride (4: NO_2 - ϕ - SO_2Cl) using nuclear quadrupole resonance (NQR) techniques were reported. These studies showed that each substituted group in the benzene ring contributes to the spin–lattice relaxation with a different and independent mechanism. The mechanisms are related to reorientations of the SO_2Cl group between unequal wells, and the modulation of the electric field gradient (EFG) caused by reorientations of the NO_2 group.

The present work was undertaken primarily to measure the temperature dependence of the chlorine NQR parameters in 3-nitrobenzene sulphonyl chloride (3: NO_2 - ϕ - SO_2Cl) as a means to investigate the characteristics of the intramolecular motions for this compound. It is well known that in nitrobenzene the presence of substituted groups in a *meta* position in the benzene ring affects the bonds in a different way to that for *para* and *ortho* substitutions. Therefore, we expected to observe a different behaviour of the chlorine NQR frequency and spin–lattice relaxation time in 3: NO_2 - ϕ - SO_2Cl to that found in 2: NO_2 - ϕ - SO_2Cl and 4: NO_2 - ϕ - SO_2Cl .

Experimental measurements of resonance frequency, ν_Q , linewidth, $\Delta\nu$, and of the ^{35}Cl and ^{37}Cl spin–lattice relaxation times, T_1 , are reported as functions of temperature. Measurements of the ^{35}Cl resonance frequency as a function of pressure are also recorded at four different temperatures.

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A brief overview of experimental procedures is given in section 2. The results are presented in section 3. The analysis and discussion of the data are given in section 4. A brief discussion constitutes section 5.

2. Experimental details

A quantity of 3:NO₂- ϕ -SO₂Cl was obtained from Aldrich Chemical Co. (#25,466-5) and used without further purification. The sample container was a cylinder of length 4 cm and diameter 1.1 cm; the amount of sample used was 5 g. The measurements were taken using a Fourier transform (FT) pulse spectrometer described elsewhere [3] in conjunction with a TECMAG acquisition system. The temperature was controlled within ± 0.1 K using a home-made cryogenic system and a Lakeshore temperature controller. The ³⁵Cl NQR frequency and linewidth were obtained from the FFT of the free induction decay after a $\pi/2$ pulse and the ³⁵Cl and ³⁷Cl spin-lattice relaxation times were determined from inversion-recovery pulse sequence measurements.

Measurements of the ³⁵Cl NQR frequency as a function of applied hydrostatic pressure were made using a probe consisting of an RF coil placed inside a cylindrical beryllium-copper pressure vessel [4]. Pressure determinations were accurate to better than ± 0.4 MPa and temperature was controlled to within ± 0.3 K.

Copper-constantan thermocouples were employed for the temperature measurements. The temperature range covered was between 60 and 150 K and the pressure range between 1 and 300 MPa.

3. Results

A single ³⁵Cl NQR line was observed for 3:NO₂- ϕ -SO₂Cl in the temperature range 60–150 K showing that all chlorine nuclei in the crystal are equivalent. The frequency of the resonance at 77 K agrees with that reported by Bray and Ring [5]. The temperature dependence of the NQR frequency is plotted in figure 1 as a function of temperature, together with the ³⁵Cl NQR frequencies of 2:NO₂- ϕ -SO₂Cl and of the α phase of 4:NO₂- ϕ -SO₂Cl. The behaviour of ν_Q in 3:NO₂- ϕ -SO₂Cl is seen to be rather different from that in the other compounds. This is not especially surprising since it is known, in general, that *para* and *ortho* substituted compounds show different behaviour than *meta* substituted compounds.

Figure 2 shows the ³⁵Cl NQR linewidth, $\Delta\nu$, as a function of temperature. It is observed that $\Delta\nu$ increases rapidly with temperature, showing a maximum at about $T = 125$ K. If only small-angle molecular librations are present, an essentially constant linewidth is expected. Since this is not the case, we conclude that a second relaxation mechanism must be present and speculate that it is related to reorientations of either the SO₂Cl group or the NO₂ group.

The temperature dependences of the ³⁵Cl and ³⁷Cl spin-lattice relaxation times are shown in figure 3. These data suggest that T_1 is not proportional to $T^{-\lambda}$ in the temperature range measured. This fact, together with the behaviour of $\Delta\nu$, provide conclusive evidence that a mechanism other than electric field gradient modulation by small-angle molecular librations is important for the relaxation. Figure 4 shows the temperature dependence of the ³⁵Cl T_1 values for the three compounds of the n :NO₂- ϕ -SO₂Cl family. It is observed that T_1 in 3:NO₂- ϕ -SO₂Cl is shorter than, and has a temperature dependence which is quite different from, that of the other two compounds.

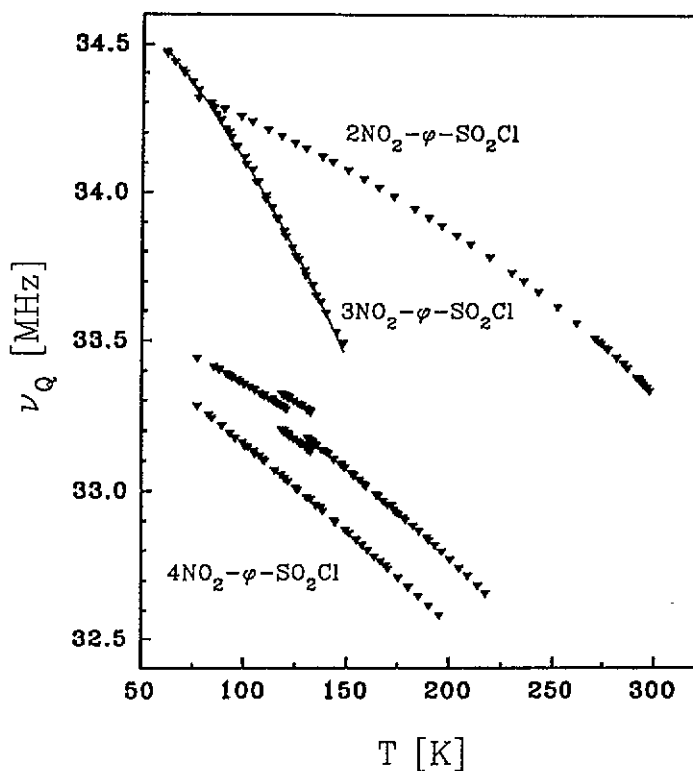


Figure 1. The temperature dependence of the ^{35}Cl NQR frequency in three compounds of the family $n:\text{NO}_2-\phi-\text{SO}_2\text{Cl}$. The solid line is the fit to the $3:\text{NO}_2-\phi-\text{SO}_2\text{Cl}$ data using equation (8).

Measurements of the ^{35}Cl ν_Q as a function of applied hydrostatic pressure in the range 1–300 MPa, for four temperatures, are plotted in figure 5. These data manifest the existence of a first-order phase transition induced by pressure.

4. Analysis and discussion

4.1. Spin-lattice relaxation time measurements

The temperature and isotope dependence of the T_1 data for $3:\text{NO}_2-\phi-\text{SO}_2\text{Cl}$ indicate that the relaxation is not caused by small-angle molecular librations alone, since T_1 is not proportional to $T^{-\lambda}$ and since $\Delta\nu$ increases with temperature in the range studied. Recalling our previous work on $2:\text{NO}_2-\phi-\text{SO}_2\text{Cl}$ and $4:\text{NO}_2-\phi-\text{SO}_2\text{Cl}$ [1, 2], it is logical to surmise that the additional mechanism is related to reorientations of either the SO_2Cl group or the NO_2 group.

Assuming that the mechanism present in addition to small-angle molecular librations is due to reorientations of the SO_2Cl group, the temperature dependence of T_1 will be given by the expression

$$1/T_1 = (1/T_1)_{\text{lib}} + (1/T_1)_{\text{reor}}. \quad (1)$$

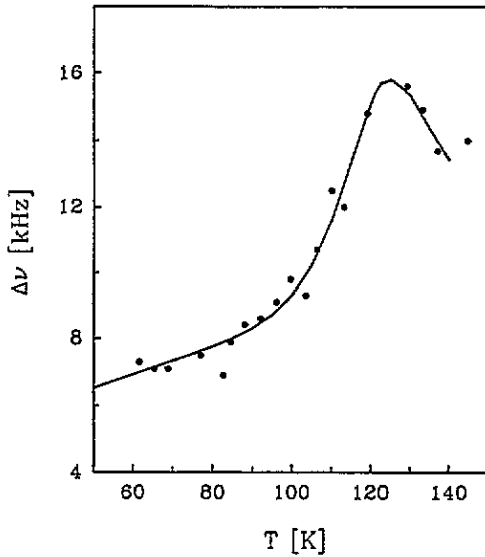


Figure 2. The temperature dependence of the ^{35}Cl linewidth in $3:\text{NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$. The solid line is a fit to the data using equation (7).

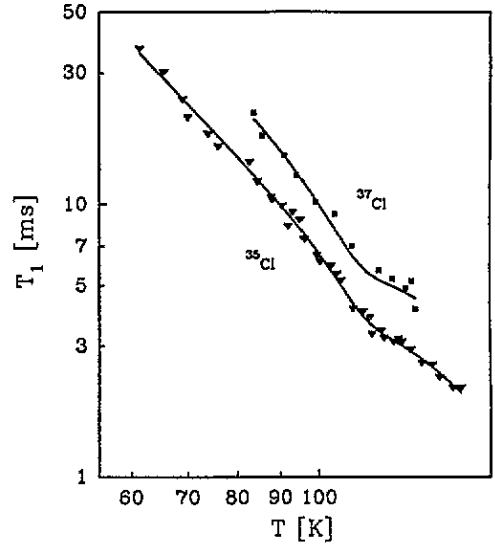


Figure 3. The temperature variation of T_1 for both chlorine isotopes in $3:\text{NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$. The solid line through the ^{35}Cl data is a fit to a model assuming reorientations of the NO_2 groups; the solid line through the ^{37}Cl data was calculated using the same EFG parameters.

Here the librational contribution obeys a power-law temperature dependence [6]

$$(1/T_1)_{\text{lib}} = bT^\lambda \quad \lambda \simeq 2 \quad (2)$$

and the contribution due to reorientations of the SO_2Cl group between unequal wells [7] has the form

$$(1/T_1) = \frac{1}{\tau} + \tau_r \quad \tau_r = \tau_{\text{or}} \exp(E_r/kT) \quad (3)$$

where E_r is the energy of the smaller barrier in the unequal potential well.

Analysis of the experimental T_1 data using equation (1) yields a value of τ_{or} of approximately 2×10^{-4} s. This is a physically unreasonable result since values of τ_{or} are typically in the range 1×10^{-14} – 1×10^{-12} s. We conclude that our initial assumption must be incorrect.

On the other hand, we will show that the observed behaviour is consistent with the existence of reorientations of the NO_2 group, in addition to small-angle molecular librations. For this case the observed temperature dependence of the relaxation rate of the chlorine nuclei is described by the expression

$$1/T_1 = (1/T_1)_{\text{lib}} + (1/T_1)_{\text{mod}} \quad (4)$$

where the modulation contribution has the form [8]

$$(1/T_1)_{\text{mod}} = \frac{1}{6} (q'/q)^2 \omega_q^2 \tau / (1 + \omega_q^2 \tau^2). \quad (5)$$

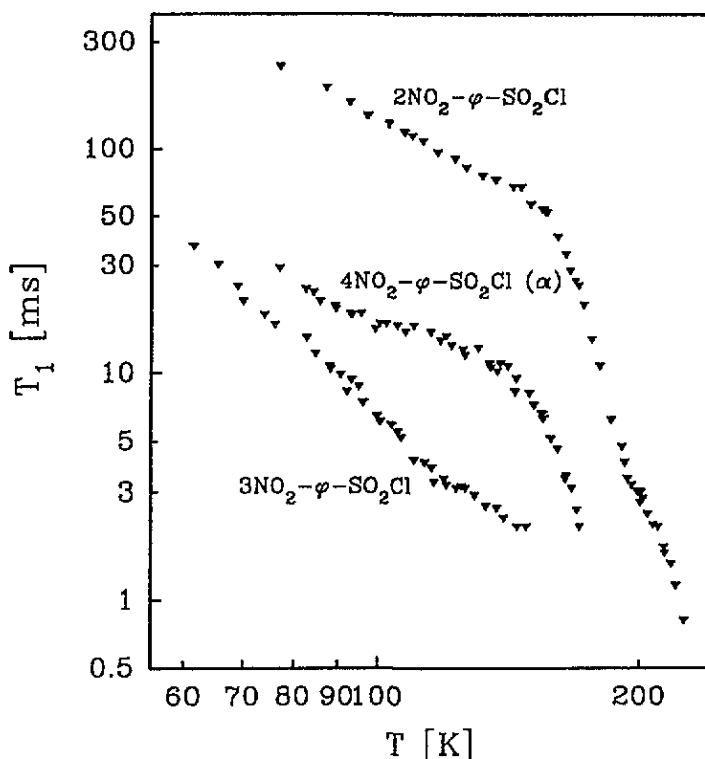


Figure 4. The temperature dependence of T_1 data for ^{35}Cl in three compounds of the family $n\text{:NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$.

In equation (5) q' is the amplitude of the moving EFG at the chlorine site, q is the full EFG at the same site, $\tau = \tau_0 \exp(E/kT)$ is the correlation time of the modulating motion, and E is the activation energy of that motion.

Using this model to fit the observed ^{35}Cl T_1 data the following values of the adjustable parameters were obtained:

$$b = 4.69 \times 10^{-8} \quad \tau_0 = 3 \times 10^{-14} \text{ s} \quad \lambda = 3.2$$

$$E = 11.7 \text{ kJ mol}^{-1} \quad q'/q = 1.8 \times 10^{-3}.$$

The best fit to the ^{35}Cl T_1 data using these values of the parameters is shown in figure 3 by the solid line through the data; the fit is quite insensitive to the value of τ_0 . Also shown by a solid line is the temperature dependence of T_1 for the ^{37}Cl nuclei. This result is calculated using the above parameters deduced from the ^{35}Cl data and values of b and ω_Q^2 appropriate for the ^{37}Cl nucleus (i.e. values for the ^{35}Cl nucleus divided by the square of the nuclear quadrupole moment ratio, namely 1.61).

Note that the fit gives a value $\lambda = 3.2$, which is significantly larger than the expected value of two. This can be explained assuming that the crystal is quite anharmonic. As shown by Zamar [9], in this case

$$1/T_1 = aT^2 + bT^3. \quad (6)$$

In the temperature range where the present study is made, $b \simeq a$ is sufficient to give $\lambda \simeq 3$ [10].

The value of the activation energy, $E = 11.7 \text{ kJ mol}^{-1}$, obtained for reorientations of the NO_2 group is of a similar magnitude to that obtained in 4: NO_2 - ϕ - SO_2Cl , namely $E = 10.5 \text{ kJ mol}^{-1}$ in the β -phase, but is significantly smaller than the value $E = 28.5 \text{ kJ mol}^{-1}$ deduced for 2: NO_2 - ϕ - SO_2Cl . This result illustrates that the presence of the SO_2Cl group close to the NO_2 group strongly contributes to the height of the barrier. The value of $q'/q = 1.8 \times 10^{-3}$ is reasonably close to the value obtained for 4: NO_2 - ϕ - SO_2Cl (0.8×10^{-3}) suggesting that the modulation effect in 3: NO_2 - ϕ - SO_2Cl is also intermolecular in origin.

4.2. NQR frequency and linewidth measurements

The observed temperature dependence of the ^{35}Cl NQR linewidth is also consistent with the assumption of reorientations of the NO_2 group. In order to observe appreciable changes in the linewidth due to reorientations of NO_2 groups, it is necessary that the condition $\Delta\nu \simeq 1/2T_1$ [11] be satisfied. The temperature dependence of the linewidth is described by the expression

$$\Delta\nu = \Delta\nu_0 + (1/12\pi)(q'/q)^2\omega_Q^2\tau/(1 + \omega_Q^2\tau^2) \quad (7)$$

where $\Delta\nu_0$, the line width in the absence of reorientations, is assumed to increase linearly with temperature. The fit yields an activation energy $E = 11.8 \text{ kJ mol}^{-1}$, in excellent agreement with the value $E = 11.7 \text{ kJ mol}^{-1}$ deduced from the T_1 data. The fit is shown by the solid line in figure 2.

We note that $\Delta\nu$ shows a maximum at $T = 125 \text{ K}$ and would therefore expect that $\omega_Q\tau \simeq 1$ at that temperature. Using the values $E = 11.8 \text{ kJ mol}^{-1}$ and $\tau_0 = 5 \times 10^{-14} \text{ s}$ deduced from the fit to the $\Delta\nu$ data gives $\omega_Q\tau \simeq 0.94$. Since $\Delta\nu$ and $1/T_1$ have the same functional dependence on τ , we would expect to observe a minimum in T_1 at $T = 125 \text{ K}$. This is consistent with the data shown in figure 3, but the actual minimum is obscured by the existence of a second relaxation mechanism, namely the librational contribution.

The temperature dependence of the ^{35}Cl NQR frequency shows the normal Bayer [12] behaviour as described by the expression

$$\nu(T) = \nu_0(1 - (3\hbar^2/2Ik\omega) \coth(\hbar\omega/2KT)) \quad (8)$$

where $\omega = \omega_0(1 - gT)$ is an average torsional frequency, ν_0 is the limiting static value of the resonance frequency, and I is the average moment of inertia of the molecule. A least-squares fit of this equation to the experimental data yielded the following parameters:

$$\nu_0 = 34\,944.3 \text{ kHz} \quad \omega_0 = 21.1 \text{ cm}^{-1} \quad g = 1.5 \times 10^{-3} \text{ K}^{-1}.$$

Note that the value of g is greater than those obtained in the other two compounds of the family [1, 2], showing that this crystal is more anharmonic.

The pressure dependence of the ^{35}Cl NQR frequency is shown in figure 5 for four temperatures. A first-order phase transition is indicated by the discontinuity and accompanying hysteresis. We see that the frequency increases linearly with pressure in both phases but note that the change is small. This is because the dominant contribution to the EFG at a chlorine site is due to the charge distribution in the chemical bond and the pressures used here are insufficient to significantly change this distribution. The primary effect of the pressure is to reduce the intermolecular distance.

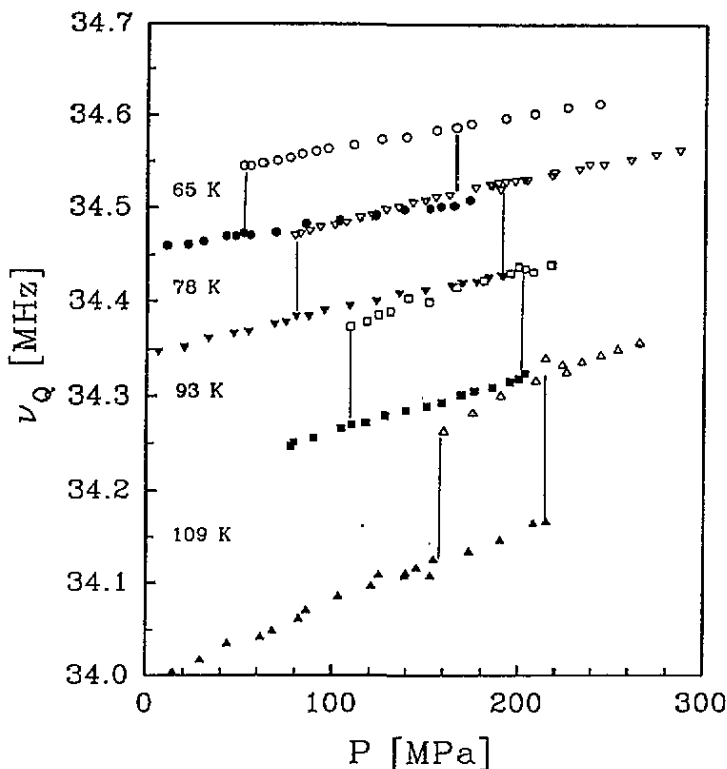


Figure 5. The pressure dependence of the ^{35}Cl NQR frequency in 3: NO_2 - ϕ - SO_2Cl at four temperatures.

Figure 6 shows the P - T diagram for the phase transition. At atmospheric pressure the transition is predicted to occur at a temperature of about 43 K. The graph shows that the phase transition pressure increases linearly with temperature for both increasing and decreasing pressure and that the hysteresis range decreases as the temperature increases. This change in the slope may be related to the onset of reorientations of the NO_2 groups. A similar effect was observed in 2: NO_2 - ϕ - SO_2Cl where, considering just the low-pressure region, the pressure dependence of ν_0 is linear and its slope increases with temperature.

5. Conclusions

Chlorine NQR measurements of the temperature dependence of T_1 and $\Delta\nu_Q$ data for 3: NO_2 - ϕ - SO_2Cl are accounted for on the basis of two competing dynamical mechanisms related to small-angle molecular librations and reorientations of the NO_2 group. No evidence for reorientations associated with the SO_2Cl group was found. The results show that this crystal is quite anharmonic. The activation energy obtained, $E = 11.7 \text{ kJ mol}^{-1}$, is of a similar magnitude to that deduced for 4: NO_2 - ϕ - SO_2Cl , but is significantly smaller than that calculated for 2: NO_2 - ϕ - SO_2Cl ($E = 28.5 \text{ kJ mol}^{-1}$). This result provides evidence that the presence of the SO_2Cl group close to the NO_2 group strongly contributed to the height of the barrier. Further, the modulation effect is quite weak, indicating that it is intermolecular in origin.

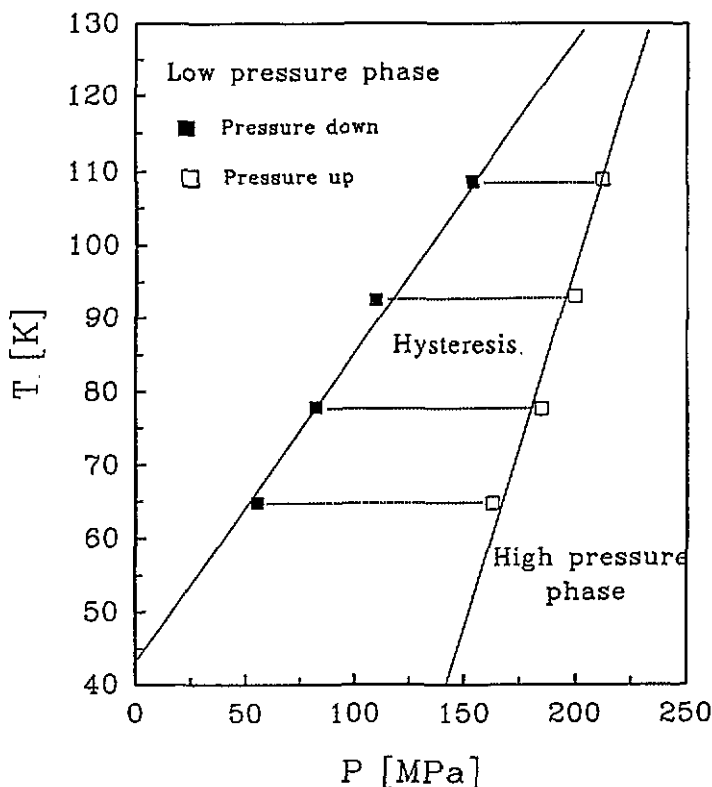


Figure 6. The P - T diagram of the first-order phase transition in $3:\text{NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$.

^{35}Cl NQR frequency measurements as a function of applied hydrostatic pressure reveal the existence of a first-order phase transition. The change in the hysteresis range with temperature is thought to be a manifestation of the onset of NO_2 group reorientations.

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