

Investigation of the Phase Transition at 67.17 K in the Thiourea-CCl₄ Inclusion Compound. As Studied by ¹⁴N NQR *

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The ¹⁴N NQR from the host lattice of the thiourea-carbon tetrachloride inclusion compound. From calorimetric measurements, two phase transitions are known to occur at 67.2 K and 41.3 K in this compound. Above the 67.2 K transition, the ¹⁴N NQR spectrum consists of one resonance, though a small splitting of about 0.5 kHz is seen at temperatures up to ca. 105 K. Below the transition, the resonance appears as a central component, in continuation of the resonance above the transition, and two satellites at +10 kHz and –8 kHz from the central line. The transition from the single resonance to a fully resolved spectrum takes place in a temperature range of less than one kelvin. The results are compared with those previously obtained with the thiourea-cyclohexane inclusion compound.

Introduction

We report on results obtained by a ¹⁴N-NQR strongly on the inclusion compound (IC) thiourea-carbon tetrachloride (Thio-CCl₄). Pure urea and thiourea crystallize in compact tetragonal and orthorhombic structures, but in the presence of long non-branched hydrocarbons they form a host lattice of parallel hexagonal channels in which the hydrocarbon guest molecules are retained. The structure of thiourea IC as host lattice is rhombohedral with symmetry R32/C. This host lattice, which cannot exist without guest molecules, can also accommodate shorter, bulky molecules with the appropriate diameter, such as cyclohexane or carbon tetrachloride.

The IC thiourea-cyclohexane (TCIC) has been studied by NQR, proton NMR, calorimetry and x-ray diffraction experiments [1]. Structural changes were observed at –124 and –144 °C. In the high temperature phase, the cyclohexane molecules reorient quite freely [1–3].

Considering Thio-CCl₄, it contains three isotopes with quadrupolar nuclei: ¹⁴N, ³⁵Cl and ³⁷Cl. Specific

heat measurements on Thio-CCl₄ [5] showed two phase transitions at 41.3 K and 67.17 K; the former appears to be first order from a sharp change in the entropy at the transition, whereas the latter seems to be second order. A ³⁵Cl NQR investigation on Thio-CCl₄ [4] gave information on the dynamics of the CCl₄ molecules. The chlorine resonances disappear just below 30 K in two steps. A CCl₄ molecule can be viewed as a tetrahedron with one face, defined by three chlorine atoms, perpendicular to the hexagonal channels of the host lattice, and the fourth chlorine atom in the axis of the host channel. A consequence of this geometrical situation is that two NQR resonance lines are observed with intensities in the ratio 1:3. Upon increasing the temperature, the first line disappears at 25.2 K, probably as a result of a tumbling motion of the CCl₄ molecules, while the second line disappears at a slightly higher temperature, 27.2 K, as a result of a rotation of the molecules around the channel axis. The low temperature at which these molecular reorientations arise conforms with the high hexagonal and tetrahedral symmetries of the host channels and the guest molecules, resulting in low potential barriers: 5.9 kJ mole^{–1} is given in [4].

As the two chlorine NQR lines disappear below 30 K, they cannot be used for investigating the transitions at 41.3 K and 67.2 K, and a ¹⁴N NQR study of the host lattice thiourea molecules was started with the aim of investigating the entire temperature range where the resonances can be observed.

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Experimental

The sample was prepared following the method reported by Sekii [5], and its composition was checked by chemical analysis and the weight loss resulting from the escape of CCl₄ molecules on exposure to the atmosphere; the sample was sealed in a glass vial.

We have used a laboratory made pulse spectrometer [6]; it is operated with data accumulation, data storage on disk and Fourier transform (FFT), and in most cases the echo signal was recorded. As there is only one phase detection on the spectrometer, the FFT spectrum is folded about the spectrometer frequency when the latter is inside the spectrum.

In the spectra thus obtained by FFT (Figures 2, 4, and 5), the frequency of the spectrometer is on the left and the lines appearing on the right are the farthest from the spectrometer frequency. Due to the frequency response of the spectrometer, their amplitude is smaller than that of lines close to the spectrometer frequency and appearing on the left; the magnitude of this effect depends on the actual extension of the spectrum and is not mentioned in the figures. The unit for the vertical axis is arbitrary, as the program just normalizes the amplitude of the spectrum. The frequency scale depends on the actual conditions of echo recording and expansion when Fourier transforming; it is shown by a two kilohertz bar on the figures. The legend below the spectra gives from top to bottom and left to right: The data file id number, the name of the compound "th CCl₄", the spectrometer frequency and the settings of the fixed, "CAPA", and variable, "CV", capacitors tuning the tank circuit, and the temperature. Only the first decimal digit of the temperature value shown is significant. The accuracy of the temperature values depends on the type of cryostat (see next paragraph); it is typically ± 0.2 K except for the helium gas cryostat where semiconductor diodes are used and the actual accuracy is of the order of ± 1 K.

The sample temperature was regulated with three different devices according to the temperature range investigated. A series of measurements was made with a variable temperature cryostat (SMC*), operated with a temperature-controlled warmed gas flow from a helium bath, to study the behaviour of the ¹⁴N-NQR in the regions of disappearance of the chlorine

resonances just below 30 K and transitions at 41.3 K and 67.17 K. The signals appearing near 2522 kHz and corresponding to the ν_+ resonance, were not good enough to permit a precise study of their structure. This is due to the small size (about 7 cc) of the sample and to the length of the rf line inside the cryostat. However, despite the small signal-to-noise ratio, it was observed that no significant changes occur in the resonance frequency at the transitions. We have also used a standard cryostat with controlled cooling by droplets of liquid nitrogen and another one with pumping over liquid nitrogen; both of them can accommodate samples of about 25 cc giving better signals than the former cryostat, and they are easier to operate.

The most significant results of the present study concern the transition at 67.2 K, a temperature easily obtained by controlled pumping liquid nitrogen, and the resonance above this transition.

Results

¹⁴N-NQR, with spin $I=1$, consists of a three line spectrum, when the asymmetry, η , of the electric field

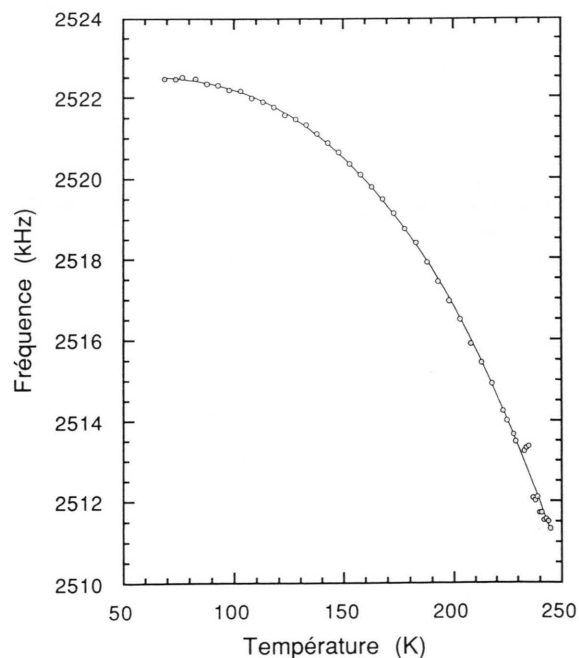
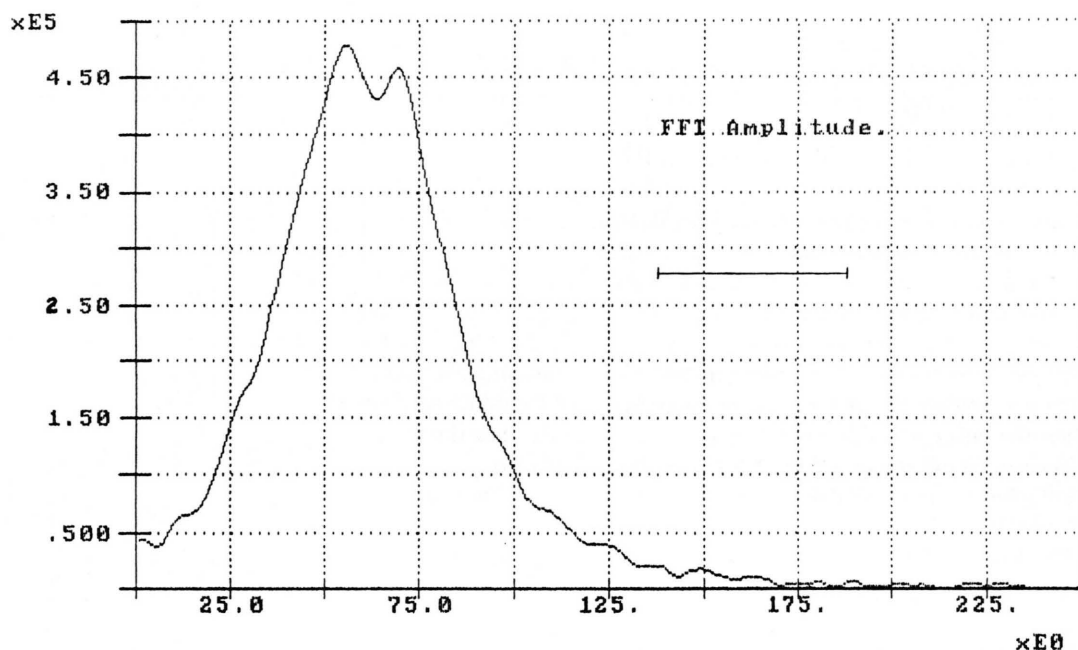


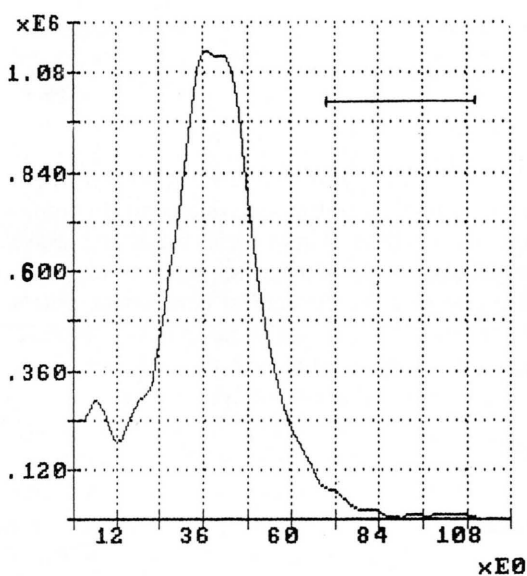
Fig. 1. ¹⁴N resonance ν_+ versus temperature above the phase transition at 67 K.

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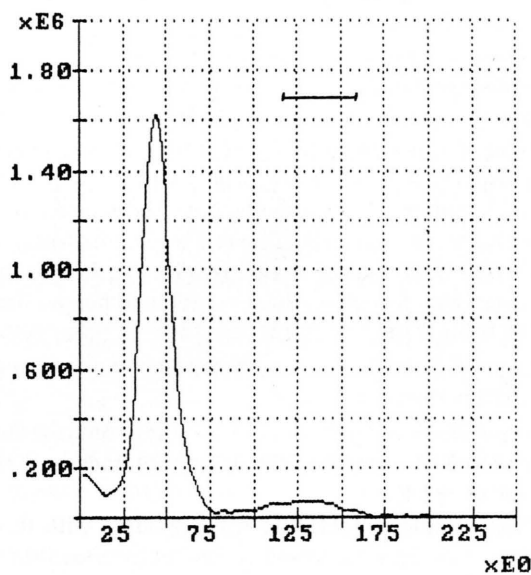


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th CCl₄

F = 02520000 Hz CAPA = 1 CV = 121
Temperature = 76.9808 K



d:\TEMP\JE_03_06\03135346.DAT
Temperature = 100.00 K
F = 02524000 Hz CAPA = 1 CV = 145



d:\TEMP\JE_03_06\03080421.DAT
Temperature = 109.9633 K
F = 02524000 Hz CAPA = 1 CV = 145

Fig. 2. a) The structure at the top of the resonance line at 77 K. b) The disappearance of the structure between 100 K and 110 K. A one kilohertz bar is shown for frequency calibration.

gradient is non zero:

$$\begin{aligned} \nu_+ &= (3 + \eta) e^2 Q q / 4h, & \nu_- &= (3 - \eta) e^2 Q q / 4h, \\ \nu_d &= \nu_+ - \nu_- = \eta e^2 Q q / 2h. \end{aligned}$$

In these expressions, $e^2 Q q$ and h are respectively the quadrupole coupling and Planck constants. The frequencies ν_+ and ν_- are typically in the range 1–4 MHz and ν_d below 1 MHz. Though ν_- in Thio-CCl₄ has been measured at 77 K, only the resonance at ν_+ has been extensively studied. The results are as follows:

Above $\simeq 67$ K a single ν_+ resonance is observed, while below this temperature the ν_+ resonance consists of three lines, the central component continuing the high temperature line. This indicates a transition and is consistent with the corresponding result of the thermodynamic study [5].

At 77 K, the resonance frequencies were found to be

$$\nu_+ = 2522.5 \text{ kHz}, \quad \nu_- = 1895.0 \text{ kHz}.$$

On increasing temperature, ν_+ can be seen up to 215 K; however, the transverse relaxation time decreases and the intensity of the echo diminishes, and the resonance can only be seen by the beats on the free induction decay following the pulses. The temperature dependence of the resonances is shown in Figure 1.

A feature worth mentioning is a structure on the line ν_+ looking like a small (0.5 kHz) splitting of the resonance which is about 1.5 kHz wide at half height (Figure 2a). This structure progressively disappears when the sample is warmed up above 100 K and is not observable above 110 K (Figure 2b). The half-height line width then reduces to 1.0 kHz. Very strikingly, no splitting was found on line ν_2 , its half-height line width being 1 kHz or slightly less, and no other resonance was detected in an extensive search above and below this resonance.

The general behaviour of the temperature dependence of the resonance frequency above 67 K is quite normal, following the trend of Bayer's theory: the frequency decreases with increasing temperature as a result of the efg-components averaging under the effect of thermal motion. However, the average reduction of the resonance frequency over the temperature range studied is only 64 Hz K^{-1} , which is much less than 330 Hz K^{-1} found for the pyrazine ν_- line at 2950 kHz [7] or 500 Hz K^{-1} for the trimethylamine ν_+ line at 3900 kHz [8]. But it differs not much from the low temperature 50 Hz K^{-1} and high temperature 110 Hz K^{-1} phase values of thiourea-cyclohexane [3].

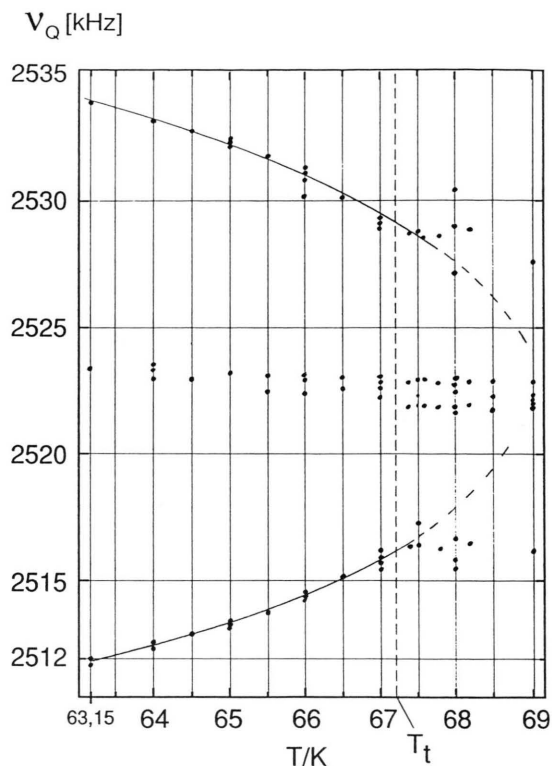


Fig. 3. The ^{14}N ν_+ resonance temperature dependence between 63 K and 69 K. The solid and dashed lines are just guides for the eye.

Below 67 K and above 63.2 K (nitrogen triple point), three lines are observed, one central component and two satellites at frequencies below and above the central component. On the frequency vs. temperature diagram (Fig. 3), the central component points are on the extrapolation of the curve $\nu_+(T)$ obtained at temperature above 67 K and the splitting of the resonance mentioned above is still observed.

The results from a first series of measurements suggested [9] that the transition at $\simeq 67$ K was first order as, on the one hand, the almost straight lines representing the temperature dependence of the high and low frequency satellites in the spectrum below the transition did not converge at the transition temperature and, on the other, the dispersion of experimental points obtained in different runs could be considered as indicative of some hysteresis effect related to the sample history.

Later, a new and more careful investigation showed that the dispersion of the experimental points in the first investigation could be highly reduced and thus

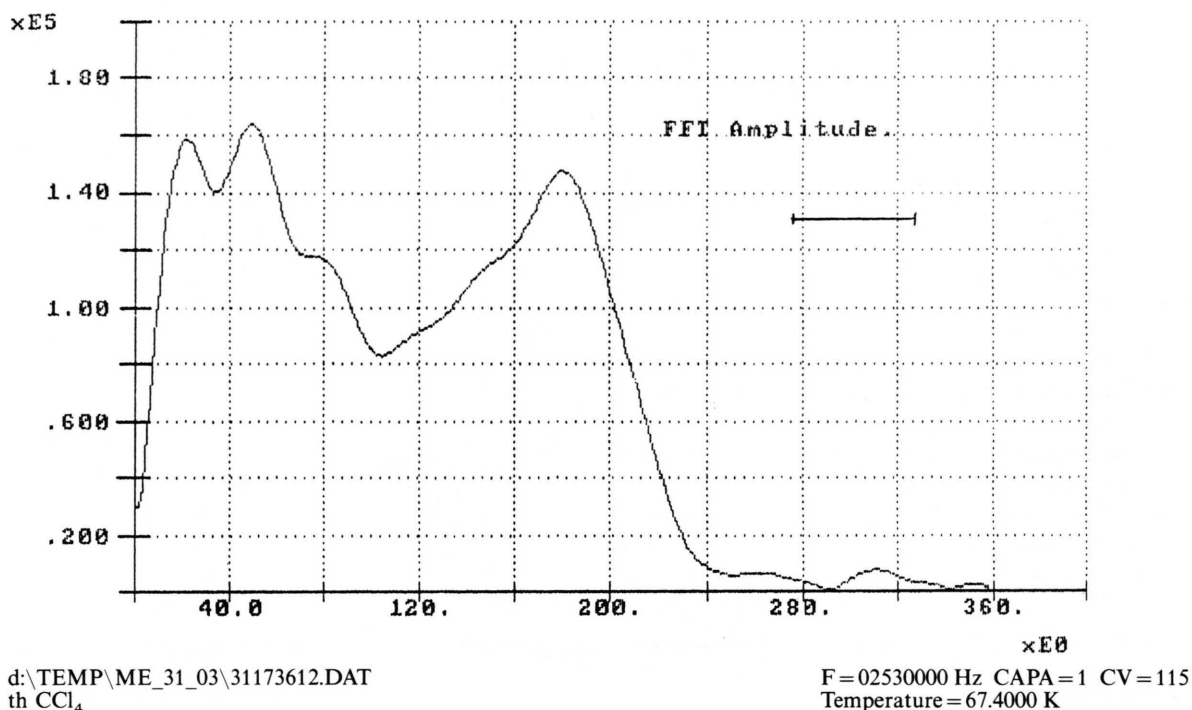


Fig. 4. Spectrum at 67.4 K with the spectrometer frequency, $\nu_s = 2530$ kHz, above the upper frequency satellite. The latter is now close to the central component and begins to mix with it.

did not result from hysteresis; the experimental points are now closer to the average continuous line that can be drawn for the temperature dependence. Concerning the variation of the spectrum near the transition, the intensity of the satellites, as compared to the central component, becomes smaller when the temperature is raised and at 67.4 K they begin to mix with the central component (Figure 4). It seems that the change of structure from three clearly separated components to one resonance takes place in a narrow temperature range of about one kelvin. At 66.5 K the spectrum is still well resolved with fully separated lines (Figure 5).

These new aspects of the temperature dependence of the NQR spectrum are consistent with the second order character of the transition as indicated by the thermodynamic study [5].

Conclusion

To conclude, at the present state of the ^{14}N -NQR investigation in Thio · CCl₄, it is possible to make a

comparison with the inclusion compound of cyclohexane in thiourea (TCIC) cited in the Introduction.

There are some similarities between the two compounds:

- Both of them show two transitions upon cooling, Thio · CCl₄, at 67.2 K and 41.2 K and TCIC at 221 K and 149 K. The lower temperatures of the transitions in Thio · CCl₄ are probably related to the higher mobility of the carbon tetrachloride molecules as compared to cyclohexane.
- The upper temperature transition seems to be second order in the two compounds and correspond to a reduction of the symmetry of the host lattice as the nitrogen atoms become nonequivalent below the transition.
- The low temperature transition is first order for both compounds, as shown from thermodynamic measurements on the CCl₄ IC and discontinuities in the frequencies in the TCIC.
- The line splittings are of the same order of magnitude, though larger in TCIC: they are about 20 kHz at 63 K for Thio · CCl₄ and 50 kHz at 77 K for TCIC.

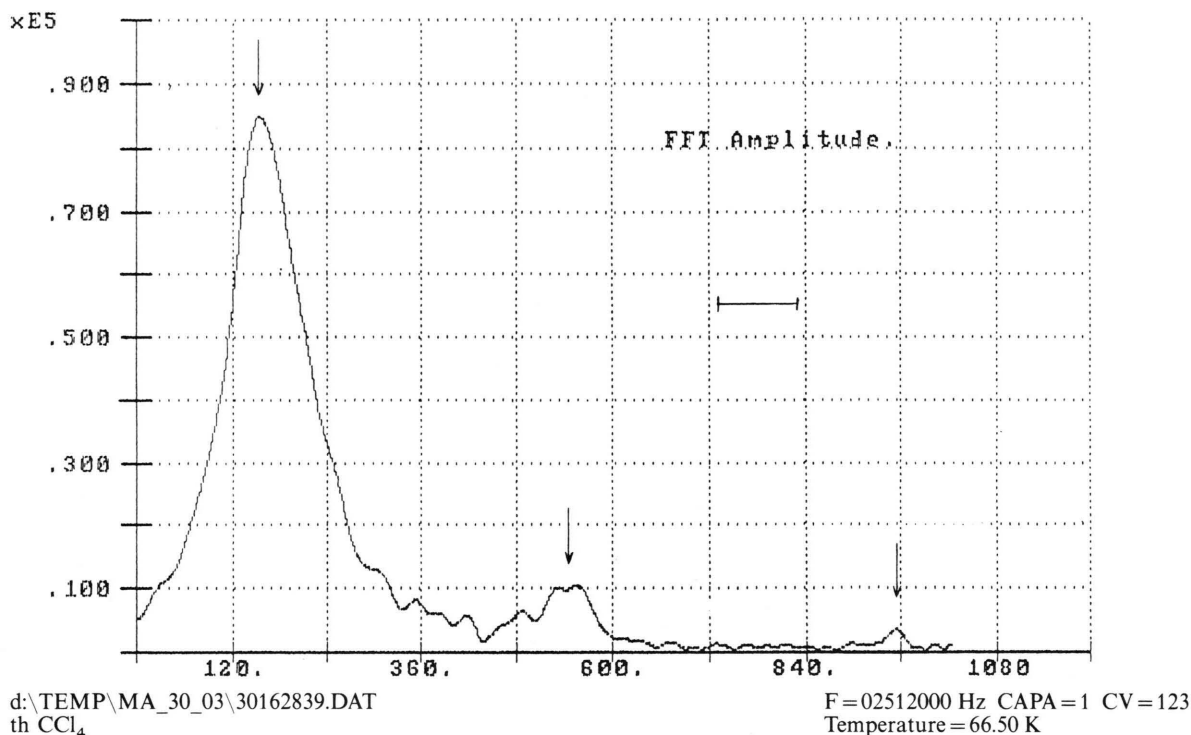


Fig. 5. Spectrum at 66.5 K with the spectrometer frequency, $\nu_s = 2512$ kHz, below the low frequency satellite; the three resonances can clearly be seen, though the intensity of the high frequency satellite, at the right of the spectrum, is quite small due to the frequency response of the spectrometer: the sensitivity is considerably reduced for resonances with frequencies far from the spectrometer frequency.

Differences are also observed:

- Whereas six lines are clearly seen in the ^{14}N spectrum in TCIC, only 3 lines are seen in Thio · CCl₄ below the 67.17 K transition.
- An unexplained splitting is observed on the ν_+ line in Thio · CCl₄ above the transition.

All these features tend to make the study of Thio · CCl₄ interesting and we hope to be able to

progress in obtaining more complete results in the future.

Acknowledgements

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