Orientational Order-Disorder and Phase Transition in Solid Trichloromethane Sulfonic Acid Chloride, Cl_3CSO_2Cl

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By DTA DSC a phase transition of Cl_3CSO_2Cl was observed, $T_{\mathrm{II,I}} = 227.4$ K, $\Delta H_{\mathrm{II,I}} = 7.10$ kJ · Mol^{-1}; $\Delta S_{\mathrm{II,I}}/R = 3.63$; $T_{\mathrm{m}} = 418.5$ K, $\Delta H_{\mathrm{m}} = 7.46$ kJ · Mol^{-1}, $\Delta S_{\mathrm{m}}/R = 2.14$. By X-ray powder diffraction, the orientationally disordered solid phase I (plastic phase) was found to be body centered cubic, Im3m, $Z = 2$, $a = 721.7$ (5) pm at room temperature. The ^{35}Cl NQR quartet fades out at the transition temperature $T_{\mathrm{II,I}} = T_{\mathrm{f}}$, and the fade out temperature T_{f} is identical for the four ^{35}Cl NQR lines. The NQR spectrum shows a hysteresis in $T_{\mathrm{I,II}} - T_{\mathrm{II,I}}$.

Introduction

Molecules with a quasispherical equipotential surface show a tendency to develop orientational disorder in the solid state. That is, under fixed center of mass, respectively center of the moment of inertia, there is a kind of premelting, coupled to a more or less random orientational disorder, and there is in most cases a pronounced transition from the ordered phase (II) to this state (phase I), which is often called the plastic phase [1].

From the viewpoint of molecular geometry one may distinguish plastic phases formed by a) tetrahedral molecules (having approximately spherical shape) b) molecules composed of two corner-connected tetrahedra with an ellipsoidal van der Waals equipotential surface, classified as octahedral molecules by Nitta [2], such as 2,2,3,3-tetramethylbutane (hexamethylethane) and c) more ore less globular molecules such as adamantane [2]. We prefer to differentiate the types of molecules forming a plastic solid phase by the van der Waals (vdW) equipotential surface: a) the group of tetrahedral-spherical molecules (e.g. CCl_4), b) the globular molecules, many cyclic, bicyclic, tricyclic hydrocarbons and aza(diaza) compounds such as 1,4-diaza-[2,2,2]-octane including octahedral molecules such as SF_6, and c) the ellipsoidal molecules. The vdW surface of the molecule is a crucial factor for the appearance of orientational disorder and a plastic phase.

$Cl_3C{-}SO_2Cl$, trichloromethane sulfonic acid chloride, is a molecule, with a slightly distorted ellipsoidal surface. The high melting point is one hint for the appearence of a disordered phase. In the following we report the phase diagram of the compound as studied by DTA/DSC, X-ray diffraction, and ^{35}Cl nuclear quadrupole resonance (NQR).

Experimental

The commercial compound (Aldrich) was used after purification by sublimation in vacuo (10 mbar). The thermodynamic data were obtained from the purified compound with Setaram DSC 121-DTA/DSC equipment. The melting peak in the DSC is rather sharp, showing very little impurity.

For the X-ray diffraction the molten sample was quenched to liquid nitrogen temperature and studied by powder diffractometry. The powder was located in 0.5 mm ∅ capillaries and examined on a STOE STADIP diffractometer (Cu$K\alpha_1$-radiation) at room temperature and at 240 K.

^{35}Cl NQR spectra were measured on a CW-spectrometer working in the superregenerative mode. For temperature control, frequency measurements etc. see [3]. The signal to noise ratio (recorder, time constant 10 s) was 10–12, decreasing slightly with increasing temperature. Near the phase transition point the intensity drops strongly. The line width was for the 4 resonances similar, around 17 kHz.

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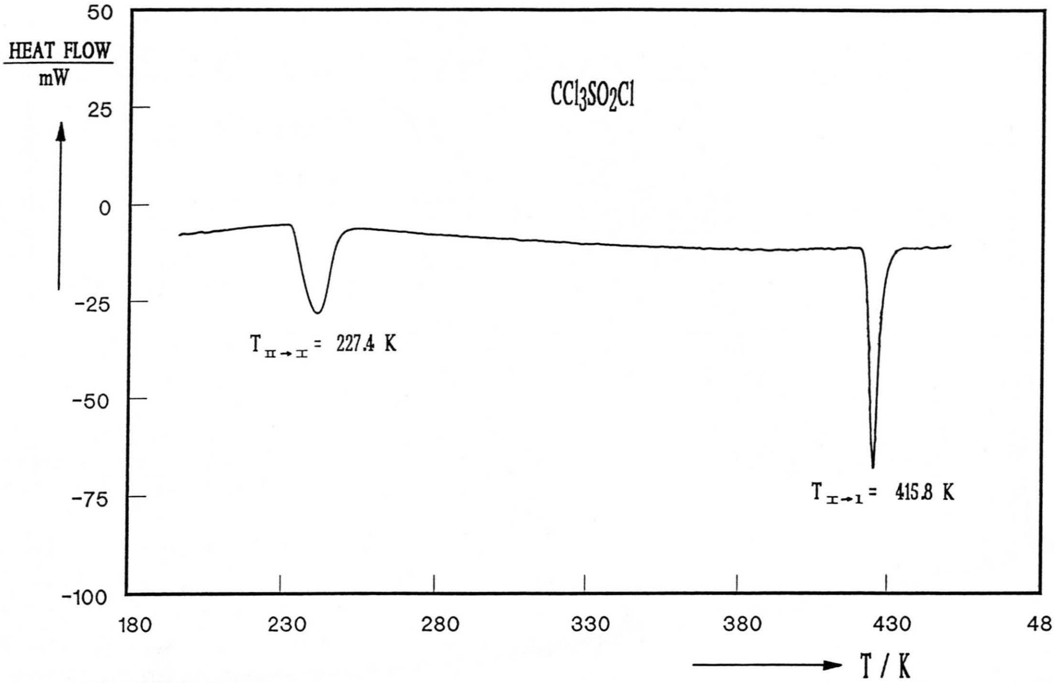

Fig. 1. DTA/DSC diagram of trichloromethane sulfonic acid chloride, Cl_3CSO_2Cl. Conditions: Heating curve from 170 K to 450 K, 3 K/min.

Results

Thermodynamics

In Fig. 1 we show the DSC diagram of Cl_3CSO_2Cl. The following thermodynamic data have been found:

$T_{\mathrm{II,I}} = 227.4$ K; $\Delta H_{\mathrm{II,I}} = 7.10$ kJ · mol^{-1};
$T_{\mathrm{m}} = 418.5$ K; $\Delta H_{\mathrm{m}} = 7.46$ kJ · mol^{-1};

$(\Delta S_{\mathrm{II,I}}/R) = 3.63$;
$(\Delta S_{\mathrm{m}}/R = 2.14$.

$S_{\mathrm{m}}/R < 2.5$ is a strong sign for the formation of a plastic phase below the melting point.

X-ray Diffraction

The *X*-ray powder diffraction diagram, taken at 295 K is shown in Figure 2. The observed diffraction maxima have been indexed with a body-centered unit cell with highest possible symmetry Im3m, $Z = 2$. The lattice constant is $a = 721.7\,(5)$ pm; $V_{\mathrm{unit\,cell}} = 375.97\,(77) \cdot 10^6$ pm^3 and for $a = 716.2\,(7)$ pm, $V_{\mathrm{unit\,cell}} = 367.42\,(19) \cdot 10^6$ pm^3 at 240 K. Results are summarized in Table 1.

^{35}Cl Nuclear Quadrupole Resonance

At 77 K the ^{35}Cl NQR spectrum of Cl_3CSO_2Cl was observed several times and discussed [4–7] in connection with the study of the bonds C–Cl and S–Cl. In Fig. 3 we show the temperature dependence of the ^{35}Cl NQR four line spectrum, which is separated into a group of three lines, belonging to the chlorines of the CCl_3 and a line at lower frequency, originating from the chlorine bonded to the sulfur atom. There is a smooth decrease of the frequencies with temperature and a common fading out of the four lines at the transition temperature $T_{\mathrm{II,I}} = 227.4$ K. In Table 2 we report the frequencies at some selected temperatures and the coefficients of the power series development

$$\nu = f(T) = \sum_{i=-1}^{2} (a_i T^i)\,.$$

The frequencies reported in [6] are 40 kHz higher, and the difference is most probably just the quench frequency. The data reported in [5] deviate from ours also in the direction of higher values.

If one considers the mean temperature dependence of the ^{35}Cl NQR resonances of the CCl_3 chlorines, the

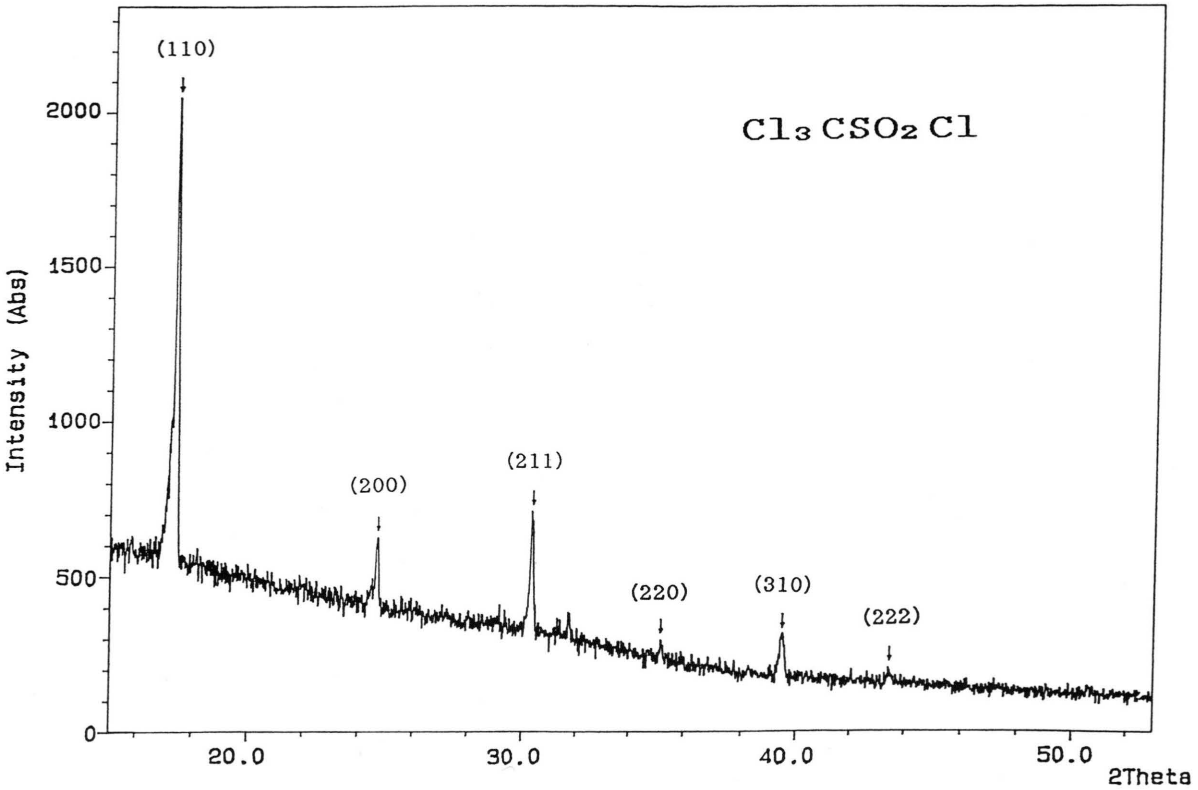

Fig. 2. X-ray powder diagram of the plastic phase I of trichloromethane sulfonic acid chloride, $T = 295$ K, CuKα radiation, Graphite monochromator (002).

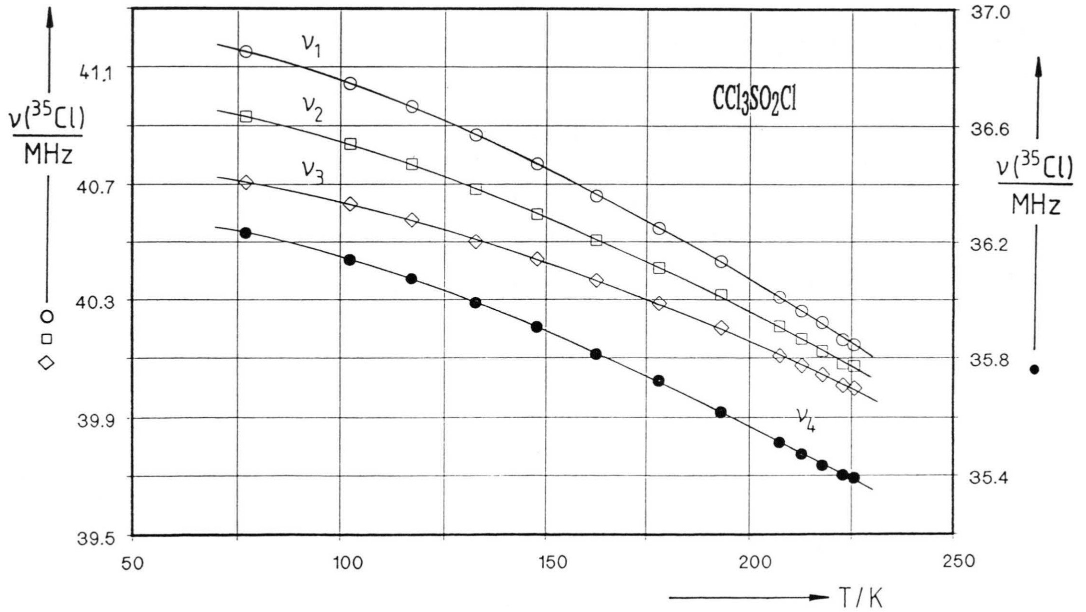

Fig. 3. Temperature dependence of the ^{35}Cl NQR spectrum of Cl_3CSO_2Cl.

frequencies decrease with increasing temperature due to the librational motions of the molecules in the lattice and the temperature coefficients being in the range for molecules in the solid state [8]; they do not show unusually strong motions in phase II.

We note that the transition phase I → phase II shows a delay in the ^{35}Cl NQR experiments. Cooling phase I from 20 °C fast (within 10′) down 10° below the thermodynamic transition temperature $T_{II,I}$, we had to wait for 1 h before the NQR signal was observable. The ordering of the disordered phase is delayed.

Discussion

From the ^{35}Cl NQR spectroscopy we find that T_f is common for the chlorine atoms of the Cl_3C group and for the SO_2Cl group of the molecule, showing that the phase transition is connected with a overall orientational disorder of the molecule. From the ^{35}Cl NQR spectrum we learn also that in phase II the symmetry of the molecule is 1. The three chlorines of the Cl_3C group are crystallographically independent. Three different bond lengths C–Cl must appear in the ordered structure. For the free molecule Cl_3CSO_2Cl intermolecular distances and angles have been determined by electron diffraction [9].

Table 1. Results of the X-ray powder diffraction of Cl_3CSO_2Cl, $T = 295$ K, CuKα-radiation. Body centered cubic, $a = 721.74(50)$ pm; $V_{\text{unit cell}} = 375.97(77) \cdot 10^6$ pm. The intensities are given in a relative scale, the intensity of the strongest reflection set to 10.

$(h\,k\,l)$	$(2\,\vartheta)_{\text{obs}}$	$(2\,\vartheta)_{\text{calc}}$	I(295 K)	I(240 K)
(110)	17.356	17.362	10	10
(200)	24.661	24.650	1.24	0.99
(211)	30.321	30.310	2.36	1.80
(220)	35.116	35.140	0.21	0.18
(310)	39.445	39.449	0.79	0.45
(222)	43.407	43.396	0.17	0.14

The plastic phase I of Cl_3CSO_2Cl has a very wide range of existence from $T_{II,I} = 227.4$ K to $T_m = 418.5$ K. A ratio $T_m/T_{II,I}$ of 1.84 is not a surprising finding for a molecular plastic crystal with ellipsoidal vdW potential surface. Comparing these data with other ellipsoidal, similarly shaped molecular compounds we find [2]:

$(CH_3)_3C{-}C(CH_3)_3$,	$T_{II,I} = 148$ K,
$Cl_3C{-}CCl_3$,	$T_{II,I} = 344.6$ K,
$(CH_3)_2ClC{-}CCl(CH_3)_2$,	$T_{II,I} = 161$ K,
$T_m = 373.7$ K,	$T_m/T_{II,I} = 2.52$,
$T_m = 458$ K,	$T_m/T_{II,I} = 1.32$,
$T_m = 434$ K,	$T_m/T_{II,I} = 2.70$.

The phase width of plastic phases composed of ellipsoidal molecules is much wider than that of tetrahedral plastic phases:

for	CCl_4	$T_m/T_{II,I} = 1.11$,
	CBr_4	$T_m/T_{II,I} = 1.13$,
	$C(CH_2OH)_4$	$T_m/T_{II,I} = 1.18$.

Acknowledgement

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Table 2. ^{35}Cl NQR frequencies at selected temperatures and coefficients of the power series expansion

$$\nu_1 = \sum_{i=-1}^{2} (a_i T^i)$$

of Cl_3CSO_2Cl. z is the number of experimental points used in the power series development and σ is the mean squares deviation. The polynom is valid in the range 77–226 K.

ν_i	$\nu(T = 77\text{ K})^{a}$ MHz	$\nu(T = 178\text{ K})$ MHz	$\nu(T = 223\text{ K})$ MHz
ν_1	41.153	40.594	40.164
ν_2	40.931	40.409	40.080
ν_3	40.706	40.285	40.006
ν_4	36.234	35.725	35.403

[a] [6], $T = 77$ K, ν_f in MHz: $\nu_1 = 41.192$; $\nu_2 = 40.971$; $\nu_3 = 40.742$; $\nu_4 = 36.276$

ν_i	z	$\frac{\sigma}{\text{kHz}}$	$\frac{a_0}{\text{MHz}}$	$\frac{a_{-1}}{\text{MHz} \cdot \text{K}}$	$\frac{a_1 \cdot 10^3}{\text{MHz} \cdot \text{K}^{-1}}$	$\frac{a_2 \cdot 10^6}{\text{MHz} \cdot \text{K}^{-2}}$
ν_1	13	3.9	41.665	−12.149	−3.596	−12.811
ν_2	13	4.6	41.238	− 8.016	−2.920	−11.122
ν_3	13	4.1	40.919	− 2.851	−1.348	−11.981
ν_4	13	4.1	36.782	−14.318	−4.066	− 8.162

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