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Analysis of Molecular Motions in $SiCl_4$ by ^{35}Cl NQR Spectroscopy

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The temperature dependence of the ^{35}Cl nuclear quadrupole resonance frequencies, spin-lattice relaxation times and line widths were analyzed for the presence of a solid-solid phase transition in $SiCl_4$. The brittle phase was verified to temperatures approaching the melting point. Evidence suggesting the formation of a plastic phase at elevated temperature is discussed.

The analysis of molecular motions by nuclear quadrupole resonance spectroscopy (NQR) is well known,[1] with many examples available in the literature.[2] The analysis is based on the examination of the temperature dependences of the NQR observables, which include the resonance frequency (ν_Q), spin-lattice relaxation time (T_1), spin-spin relaxation time (T_2) and line width ($\Delta\nu_{1/2}$). These quantities are used to characterize solid-solid phase transitions and activated rate processes such as those caused by molecular reorientation. The molecular dynamics of the Group IV halides are particularly suited to analysis by NQR because in this series of compounds all the halides, with the exception of F, possess nuclear angular momenta I greater than 1/2, which are of high natural abundance and concentration. In addition to their well known physical properties (Table 1), the Group IV halides exhibit both brittle and plastic phases. They also have important industrial applications e.g. the extensive use of polychlorosilanes in the electronics industry to facilitate the fabrication of high purity Si wafers.[3]

Recently, Nakayama, Nakamura, and Chihara[4] (NNC) analyzed the brittle-plastic phase transition in the series MX_4 (where M=C, Si, Ge, Sn and X=F, Cl, Br, I) in terms of a long range intermolecular order parameter. Using the ratio $R=r(M)/r(X)$ for the effective atomic radii for the central atom (M) and the halide ligand (X), the NNC model predicts that for R greater than 0.24, the molecule exhibits plastic crystal formation (see Table 1).

In the Group IV chlorides only CCl_4 (R=0.17) is reported to form a plastic phase. The fact that $SiCl_4$ (R=0.24) borders the region of plastic phase formation suggests that the study of its NQR temperature dependence is ideally suited to test the NNC model. The ability of $SiCl_4$ to overcome long range ordering forces and obtain hindered rotation determines its ability to form a plastic phase. By measuring the temperature dependence of the spin-lattice relaxation time (T_1), the barrier to molecular reorientation for $SiCl_4$ in the solid phase is obtained and compared with previously reported results on $GeCl_4$ which does not exhibit plastic phase formation.

Table 1. Physical Constants for the Group IV Chlorides

Compound	T_m	Bond length	Force constant	$r(M)/r(X)$
	K	nm	mD nm^{-1}	
CCl_4	250.0	17.7	3.6	0.17
$SiCl_4$	203.0	20.1	2.7	0.24
$GeCl_4$	223.5	20.8	2.7	0.32
$SnCl_4$	237.0	23.1	2.5	0.41

Experimental

The $SiCl_4$ samples were purchased from Alfa Chemicals (Ultrapure) and zone purified. The melting points of the pure samples were recorded as a temperature range, from 203.2K through to 203.4 K. The liquid samples were ampouled in 40 mm×22 mm glass vials which were used in situ in an appropriately designed sample coil. The samples were slow- cooled in situ over a 48 hour period to a final temperature of 77 K, and annealed at this temperature for an additional 24 hours.

NQR temperature dependent measurements were made using a pulsed spectrometer previously described.[5] Single $\pi/2$ pulse experiments were used to measure $\Delta\nu_{1/2}$; inversion recovery $\pi-\tau-\pi/2$ pulse sequences were used to measure T_1; and a modified Hahn spin echo $\pi/2-\tau-\pi$ pulse sequence[5] was used to measure T_2. Variable temperature control was obtained using a simple liquid nitrogen cryostat kept constant to 0.1 K as measured by a Cu-constantan thermocouple and ReX-P100 programmable temperature controller.

Results and Discussion

From the analysis of the ^{35}C NQR resonance frequency ν_Q versus T, no solid-solid phase transition was observed in $SiCl_4$. The smooth monotonic decrease of the resonance frequency as a function of increasing temperature indicates "normal" Bayer temperature dependence (Fig. 1). An additional qualitative feature of the temperature curve includes a "fade-out" of the resonance line above approximately 184 K. The high purity of the $SiCl_4$ samples eliminates the effect of impurities as the cause of the "fade-out."

The four physically inequivalent Cl sites in the $SiCl_4$ molecule give rise to four resonance lines. At 77 K, three closely spaced lines, with frequencies

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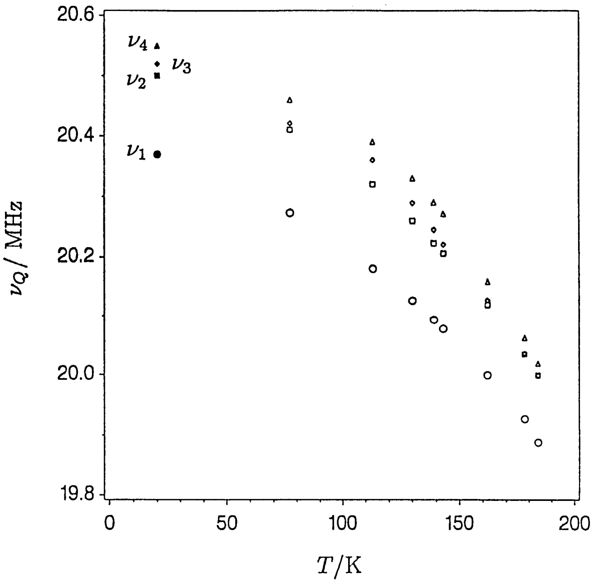

Fig. 1. ^{35}Cl NQR frequency temperature dependence in SiCl$_4$. The solid points are from Ref. 6. T_m=204 K.

ν_2=20.4090 MHz, ν_3=20.4156 MHz, and ν_4=20.4639 MHz, and a single line with frequency ν_1=20.2728 MHz, are observed. (Error in ν_Q is below ±150 Hz). These low temperature resonance frequencies are in excellent agreement with values of ν_Q previously reported at this temperature.[6] An unexpected shift exclusive to the ν_1 line was observed with increasing temperature. However, over the range of temperature investigated the frequency dependence on the temperature is Bayer-like. In addition, the average $\nu_Q(T)$ behaves linearly in T^2, confirming a recently reported observation on the behavior of $\nu_Q(T)$ in compounds which exhibit Bayer-like temperature dependences.[7] The dependence of $\nu_Q(T)$ on T^2 was useful in extrapolating the low temperature resonance frequencies to predict the high temperature resonance frequencies.

The nature of the distorted tetrahedral geometry in the Group IV halides may lie in their topology. Both the gas and liquid phases of the Group IV halides exhibit molecular structures which are perfect tetrahedra, with 4 equal M-Cl bond lengths. However, upon solid phase formation the molecules distort slightly, creating their experimentally observed distorted tetrahedral geometry. This distortion is observed as a split in the resonance frequency in the NQR spectrum. The similarity of the splitting pattern (high frequency triplet followed by a low frequency singlet) in the series SiCl$_4$, GeCl$_4$, and SnCl$_4$ suggests that the crystal structures of these compounds are isomorphous. An NQR Zeeman study[8] on a GeCl$_4$ reported a distorted tetrahedron (D_{2h}) crystal structure. However, a recent evidence[4] suggests that the structure is of the P2$_1$/c space group, agreeing with an earlier X-ray crystallographic structure determination of SnCl$_4$.[4] It is therefore reasonable to assume that the crystal structure for SiCl$_4$ is P2$_1$/c. The inability of tetrahedra to space fill is well known and leads to frustration upon crystal formation.[8] Distortions in the tetrahedra, as in Frank-Kasper phases,[9] relax frustration to enable efficient molecular packing. The evidence of a distorted tetrahedral phase in solid SiCl$_4$, GeCl$_4$, and SnCl$_4$ is therefore not surprising and strongly suggests that a relaxation mechanism of the Frank-Kasper type is present in this series of compounds. For spin I=3/2 nuclei (e.g. ^{35}Cl), measurement of $\nu_Q(T)$ gives a temperature dependence which is the combined effect of both the quadrupole coupling constant (e^2Qq) and the asymmetry parameter (η). The low temperature (T=77 K) Zeeman study on GeCl$_4$ sited above, gave the average asymmetry parameters for the two groups of Zeeman split lines: η=0.035 and η=0.078. Therefore, it is expected that the asymmetry parameter in SnCl$_4$ will be small and assumed negligible particularly at high temperatures. This assumption makes $\nu_Q(T)$ a direct measure of e^2Qq.[10]

The temperature dependence of the spin-lattice relaxation time T_1 is recognized as a powerful probe to study both intra- and intermolecular dynamics.

Table 2. ^{35}Cl NQR Relaxation Times and Line Width in SiCl$_4$ 77 K

Line	ν_Q / M Hz	T_1 / ms	T_2 / µs	$\Delta\nu_{1/2}$
ν_1	20.2726	155	1.5	1461
ν_2	20.4103	113	1.7	1363
ν_3	20.4211	110	1.6	1406
ν_4	20.4598	125	1.6	1326

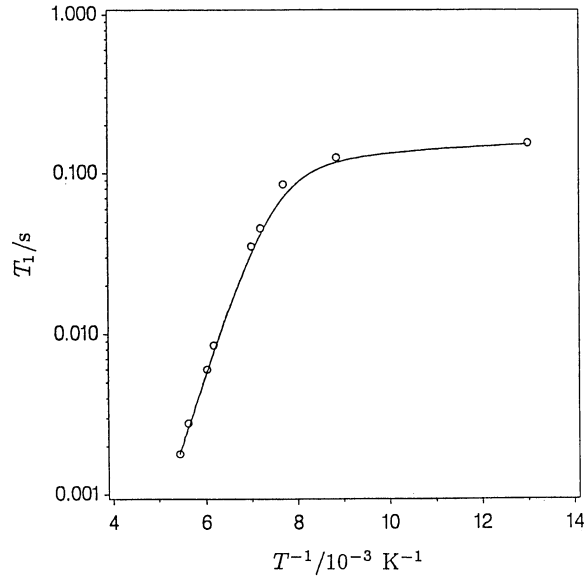

Fig. 2. ^{35}Cl NQR spin-lattice relaxation for the ν_1 line of SiCl$_4$. The solid line is a least squares best fit of Eq. 1.

Spin-lattice relaxation times for each resonance line were easily measured at 77 K because the resonance lines are sufficiently separate (Table 2). At this temperature, T_1 remains nearly constant for each inequivalent Cl atom, which suggests identical relaxation mechanisms for each of the local Cl sites. At elevated temperatures, T_1 measurements become ambiguous because the resonance lines coalesce. The ν_1 resonance line, however, remains approximately 0.1 MHz below the ν_2—ν_4 lines. Since the free induction decay (FID) of the isolated ν_1 resonance remained unperturbed by the high frequency triplet throughout the range of temperatures investigated, it was used to measure T_1 in $SiCl_4$. The temperature dependence of the ν_1 line (Fig. 2) changes rapidly at temperatures above approximately 160 K. The general behavior is characteristic of the onset of either rotational or translational motion.[11] Because contributions from translational motions to spin-lattice relaxation are generally small,[11] the increase is attributed to molecular rotations only.

At low temperatures (<160 K), the T_1^{-1} temperature dependence is linear in T^2. Van Kranendonk[12] showed that at low temperatures, anharmonic Raman processes, which obey a T^{-2} temperature dependence, dominate NQR spin-lattice relaxation. From this result, a well known phenomenological expression was derived to model the temperature dependence of T_1:

$$T_1^{-1} = AT^2 + K\exp(-E_a/RT), \tag{1}$$

where A and K are constants, discussed below, and E_a is the activation energy to overcome the potential barrier to some, undefined, molecular reorientation. This model follows the standard Arrhenius model for an activated process.[13] The validity of Eq. 1 has been corroborated by other methods (e.g. DSC, NMR and rotational/vibrational spectroscopy).

In the present work, low and high frequency limits to Eq. 1 were used to calculate least squares best fits for the low and high temperature T_1 data. Below approximately 145 K, T_1 is inversely proportional to T^2 with $A=1.278\times10^{-3}$ Hz K^{-2}. At temperatures above approximately 145 K, T_1 rises rapidly following an exponential behavior with a pre-exponential constant $K=4.0\pm0.8\times10^7$ Hz and an activation energy $E_a=17.1\pm0.5$ kJ mol^{-1}. The "fade-out" phenomenon mentioned above precluded measurement of T_1 above 184 K. The $SiCl_4$ reorientation activation energy is well below the activation energy reported for $GeCl_4$ ($E=63.5$ kJ mol^{-1}),[4] approximately equal to the that of hexamethylenetetramine (HMT) ($E_a=19.3$ kJ mol^{-1}),[11] which does not exhibit a plastic phase, and well above that of α-adamantane ($E_a=3.08$ kJ mol^{-1}),[11] which does exhibit plastic phase formation. If the purely rotational model is correct and the Chihara[14] model for this activation process is used, the temperature necessary to facilitate molecular reorientation would be in excess of $T=275$ K.

At this point, a discussion of the correlation time (τ_c) temperature dependence is warranted, since values for τ_c at the brittle-plastic phase transition for other molecules are available for comparison. Alexander and Tzalmona[15] (AT) successfully modelled molecular motion in hexamethylenetetramine (HMT), by assuming an isotropic sudden jump process between four nearly equivalent tetrahedral sites. The AT model has been extended, with continued success, to include many other molecular systems. It is applied here to interpret molecular reorientations in $SiCl_4$. The correlation time for the sudden jump model (τ_c) is given by

$$\tau_c \approx \frac{3}{4} T_1. \tag{2}$$

A least squares fit of the high temperature data points is used to extrapolate to correlation times near the melting point. For temperatures above approximately 197 K, correlation times fall below 10^{-9} s. Brittle-plastic phase transitions are characterized by correlation times between 10^{-9} and 10^{-11} s.[11] This suggests that a critical temperature T_c equal to approximately 197 K, can be defined, which signifies the onset of a rapid decrease in intermolecular correlation and plastic phase formation.

The extrapolated value of T_c coupled with the fade-out of the resonance line, suggests the presence of a solid-solid phase transition. It is assumed to be of the brittle-plastic phase variety. Error analysis of the high temperatures τ_c's gives a standard deviation of 3% in T (i.e. 197 ± 6 K). This value clearly overlaps with the melting point of $SiCl_4$, $T_m=203.4$ K. The error in T_c certainly questions the basis of any prediction based on comparisons of it and T_m. However, a strong case can be made. $SiCl_4$ is a globular molecule, a nearly perfect tetrahedron, and therefore serves as an excellent candidate for plastic phase formation. Arguments supporting the creation of a plastic phase may begin as follows: Weak van der Waals type forces are known to predominate the intermolecular forces in solid $SiCl_4$. As a result, low temperature T_1 data is a measure of the *intramolecular* degrees of freedom. At low temperatures (<160 K), long-range order is significantly strong enough to prevent the formation of a plastic phase. However, at temperatures approaching the melting point, long-range order becomes negligible as the molecule overcomes some barrier to hindered reorientation.

The temperature dependence of the resonance line width ($\Delta\nu_{1/2}$) was analyzed in an attempt to corroborate the activation energy determined by the spin-lattice relaxation measurements presented above. The line widths were measured as the full line width measured at half maximum amplitude (Table 3). The line width findings were less than encouraging and not at all unexpected. The qualitative analysis

Table 3. Experimental ^{35}Cl NQR $\Delta\nu_{1/2}$ and Least Squares Best Fits of Gaussian and Lorentzian Line Shape Functions in $SiCl_4$ in Hz

T/K	Exp't.	Gaussian	Lorentzian
77	1461	1454	1136
113	1497	1460	1173
130	1532	1494	1166
139	1554	1546	1227
143	1582	1577	1276
162	1801	1750	1381
166	1873	1857	1467
178	2044	1986	1558
184	2176	2150	1705

shows line widths which increase monotonically with increasing temperature. (At 77 K, $\Delta\nu_{1/2}=1461\pm50$ Hz and increases to 2176 ± 120 Hz at 184 K). Least squares best fits performed on a minimum of 350 spectral data points, at each temperature were calculated under the assumption of both a Gaussian and Lorentzian line shape function. The results indicate that throughout the temperature range the line widths are predominantly Gaussian in character (Table 3). The dominance of Gaussian character suggests that a significant dipolar broadening mechanism[16)] is present. However, the ability to determine the exact nature of the line shape is clouded by the influence of additional static and dynamic effects which are difficult to quantify[17)] and the exact mechanism is certainly in doubt.

It is no less reasonable to assume that the line width broadening mechanism is due to an increase in the molecular degrees of freedom for some activated process, leading to molecular reorientation. According to Ayant,[18)] molecular reorientations additionally broaden of the resonance line, the contribution, of which, increases with increasing temperature. Ayant proposed an Arrhenius process for the molecular reorientation:

$$\Delta\nu_{1/2}=\nu_0 \exp(-E_a/RT), \tag{4}$$

where $\nu_0=2/\pi\tau_0$. τ_0 is the correlation time of the ground vibrational state. An activation energy $E_a=1.6\pm0.1$ kJ mol^{-1} was calculated from a least squares fit of the high temperature data. The large discrepancy in E_a's obtained from T_1 analysis and those from analysis of $\Delta\nu_{1/2}$ is not at all surprising. It is well known that activation energies obtained from $\Delta\nu_{1/2}$ analysis underestimate the value of E_a.[1)]

Experimental evidence coupled with topological arguments suggests that a plastic phase is present in $SiCl_4$. However, topology alone cannot govern the crystalline phase[19)] and the nature of the chemical bonding between the molecules must be examined. The NNC model attempts to correlate these intramolecular forces with ionic ratios. As mentioned previously, the NNC model predicts plastic phase formation in Group IV halides with metal to ligand ratios less than 0.24, under the assumption of an effective ion radius.[20)] $SiCl_4$ is a borderline case and as such, should provide a means of testing the model. The activation energy to hindered rotation is sufficiently high to prevent formation of a plastic phase. The NQR analysis of the molecular dynamics in $SiCl_4$ confirms the brittle phase of $SiCl_4$ up to approximately 194 K, where evidence of a possible brittle-plastic phase transition was observed. The barrier to molecular reorientation $E_a=17.1\pm0.5$ kJ mol^{-1} is sufficiently high when compared to compounds which exhibit plastic phases to confirm the absence of a plastic phase in $SiCl_4$. However, near the melting point the correlation times change dramatically which, coupled with the observation of a resonance frequency fade-out above, suggests that a plastic phase will occur in $SiCl_4$ at these elevated temperatures, just below the melting point ($T_m=203.4$ K).

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