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Molecular Motion in $GeCl_4$ as Studied by ^{35}Cl Nuclear Quadrupole Resonance

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Temperature dependence of ^{35}Cl nuclear quadrupole resonance frequencies and quadrupole relaxation time was measured of $GeCl_4$ in the metastable phase. Above 160 K, molecular reorientation is seen active; its activation energy is 63.5 kJ mol^{-1}. This energy probably prevents $GeCl_4$ from undergoing a rotational phase transition.

Although a series of molecules MCl_4 (M=C, Si, Ge, Sn) are nearly globular assuming Td symmetry in gas phase, they do not solidify into plastic crystal except CCl_4[1] nor undergo any solid–solid phase transitions.[2–4]

In a series of works on the dynamical properties and the stability of plastic crystals, we recognized that $GeCl_4$ shows an interesting thermal behavior: This material was reported to crystallize into two phases, stable and metastable, although the condition of the preparation of each phase has not been established. The stable phase melts at 223.7 K and the metastable phase melts at 221.4 K.[5] In the heat capacity measurements[6] of the so-called metastable phase of this compound an exothermic phenomenon was observed near its melting point which appeared to be a kind of relaxation. This thermal effect may be a manifestation of some phase properties similar to the case of carbon tetrachloride[7] where the metastable cubic phase is transformed into the stable rhombohedral phase spontaneously. Such consideration led us to study of the temperature dependence of the NQR frequencies and of the spin-lattice relaxation times in $GeCl_4$.

Experimental

Commercially available specimen of $GeCl_4$ (Soekawa Chemical Co., Ltd, stated purity 99.999999%) was vacuum distilled and sealed in a glass ampoule with 13 Pa He gas. This sample is of the same origin as that used for the previous heat capacity measurements.[6]

All the measurements were made using a MATEC pulsed spectrometer system by the FT method to determine the frequencies of three closely spaced resonance lines, the error being ±0.2 kHz. The nuclear quadrupolar spin-lattice relaxation time T_1 was measured with the $\pi/2-\tau-\pi/2$ method with an estimated error of ±10 percent.

The temperature dependence was determined by using a simple cryostat with liquid nitrogen as the refrigerant. The temperature was kept constant within ±0.1 K during the measurement and measured with Chromel-P vs. Constantan thermocouples, calibrated against the standard platinum resistance thermometer.

Results and Discussion

In our experiment only one of the two phases reported so far could be obtained by both rapid quenching and slow cooling. The solid samples prepared by different cooling rates gave the same NQR spectrum and their melting points were 221.6 K. Therefore, we identified our specimen as the "metastable phase."

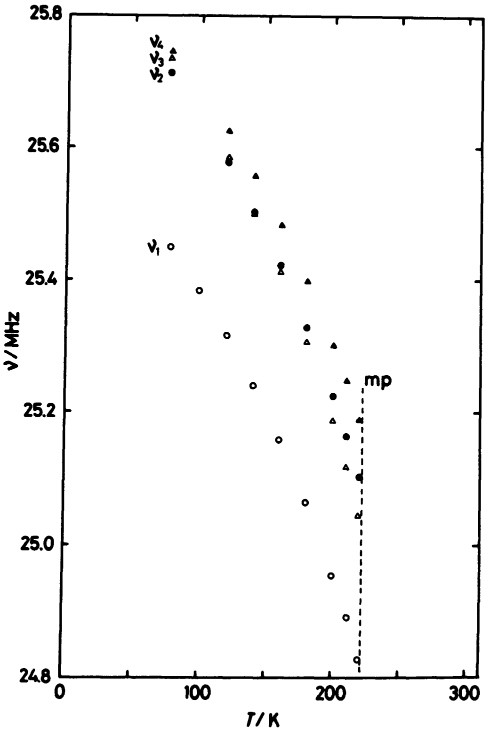

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in $GeCl_4$.

Four ^{35}Cl nuclear quadrupole resonance lines were observed at 77 K and their frequencies (ν_1=25.4491 MHz, ν_2=25.7131 MHz, ν_3=25.7356 MHz, ν_4=25.7463 MHz) agree with those reported by S. Sengupta et al.[8] within ±0.2 kHz. Temperature dependence of the resonance frequencies is shown in Fig. 1.

At around 120 K only three resonance signals are observed because of accidental overlap of two of the resonance lines. The NQR signals broadened above 210 K and disappeared just below the melting point. This broadening is induced by the molecular reorientation as will be discussed later.

Because the upper three resonance lines (ν_2, ν_3, and ν_4) occurred in a very narrow frequency range, their spin-lattice relaxation times could not be measured accurately. The temperature dependence of the spin-lattice relaxation time for the lowest resonance line

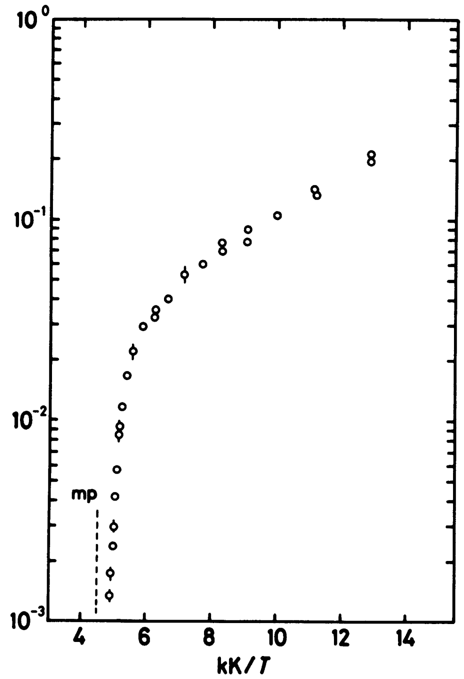

Fig. 2. Temperature dependence of ^{35}Cl spin-lattice relaxation time for the line ν_1 in GeCl$_4$.

(ν_1) is shown in Fig. 2. The plot of the relaxation rate T_1^{-1} vs. T^2 gives a straight line below 160 K, suggesting that the librational motion[9] of GeCl$_4$ molecules governs the spin-lattice relaxation below 160 K. Above 160 K a sharp decrease in the spin-lattice relaxation time was observed due to molecular reorientational motion.[10] The spin-lattice relaxation time T_1 can be reproduced by the expression

$$T_1^{-1}/\mathrm{s}^{-1} = 9.77\cdot10^{-4}\cdot(T/\mathrm{K})^2 + 1.30\cdot10^{19}\exp(-63.5\,\mathrm{kJ\,mol^{-1}}/RT). \quad (1)$$

The first term is the contribution of librational motion of the molecule, which is dominant below 160 K. The second term is brought about by the molecular reorientation with the activation energy of 63.5 kJ mol^{-1} and is dominant above 160 K. The correlation time, τ_c, can be related to T_1 by assuming an isotropic sudden jump process between four nearly tetrahedral sites as[10]

$$\tau_c \simeq (3/4)T_1. \quad (2)$$

The τ_c thus obtained is plotted in Fig. 3 as a function of the reciprocal temperature; it gives the pre-exponential factor τ_0 a value of $5.76\cdot10^{-20}$ s. The correlation time, τ_c, at the melting point is $5.4\cdot10^{-5}$ s.

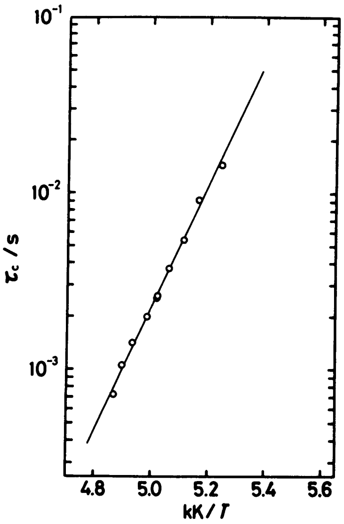

Fig. 3. Temperature dependence of the correlation time for the overall rotation in GeCl$_4$.

In globular molecules having tetrahedral or octahedral symmetry, which show plastic phases, the correlation time of the molecular overall reorientation at the brittle-plastic phase transition lies usually in the range between $7\cdot10^{-9}$ and 10^{-11} s,[11-14] whereas, τ_c for GeCl$_4$ is as long as 10^{-5} s even at the melting point. This fact shows that in GeCl$_4$ the molecular reorientation is not so sufficiently excited that the crystal undergoes a rotational transition to a plastic phase even at the melting point. If we use the empirical relation[15] $E_r=\alpha\cdot R\cdot T_c$ to derive the hypothetical rotational transition point T_c from the rotational activation energy E_r, the rotational transition would not occur until about 1000 K is reached, using $\alpha=7.5$ for the brittle phase.[15] Although the origin of the very high E_r is not known at the present stage, it prevents the GeCl$_4$ crystal from undergoing a rotational transition despite the fact that the each molecule is globular.

As mentioned in the introduction, an interesting thermal relaxation was observed above 190 K during the heat capacity measurements.[6] Thus, a small but distinct exothermic phenomenon occurs with a time constant of 40 min at 190 K, 2 h at 200 K and 10 h at 210 K. Hence we attempted to detect some effect of such a thermal relaxation phenomenon on the NQR parameters. Because of the very long (≈700 μs) free induction signal and short T_1 (≈1 ms) it was not possible to measure T_1 above 205 K. We, therefore, searched for a possible change of the ^{35}Cl NQR line shape with time: At 200, 205, 210, and 212 K, any variation of the line shape was not detected during twice the thermal time constant in each temperature. The reason why NQR did not see the corresponding anomaly is not apparent at present.

Among MX$_4$ compounds (M=Si, Ge, Sn; X=halogen), SnCl$_4$[16] and SnBr$_4$[17] show $P2_1/c$ structures with $Z=4$. The unit cell contains four crystallographically inequivalent halogen atoms. These two compounds as well as most of other tetrahalo compounds including GeCl$_4$ give similar NQR spectra, i.e., there are four NQR lines[18,19] of which three higher frequency lines are closely spaced and the lowest frequency line is far removed from the three upper lines. Thus, the NQR

Table 1. Values of the Ratio of Atomic Radii

	F	Cl	Br	I
C	0.24	0.17	0.16	0.14
Si	0.34	0.24	0.22	0.19
Ge	0.45	0.32	0.29	0.26
Sn	0.58	0.41	0.38	0.33

spectrum of GeCl$_4$ suggests strongly that the crystal assumes the crystal structure isomorphous with SnCl$_4$ and SnBr$_4$, i.e., $P2_1/c$. A recent Zeeman NQR study of GeCl$_4$[7] claimed that the metastable phase is orthorhombic with *mmm* or D_{2h} symmetry. Close examination of the result of their Zeeman effect study reveals, however, that the direction cosines of the twelve principal *Z* axes of the EFG (electric field gradient) could be classified into two sets: The angles between the principal *Z* axes of equivalent chlorines were calculated to be 124, 140, and 121°, for each set, corresponding to those in SnBr$_4$[16] and SnCl$_4$,[15] i.e., 125, 140, and 125° according to the X-ray structure data. The Zeeman effect data may well be interpreted by the $P2_1/c$ structure if the single crystal used in their experiment happened to have a twin texture.

It is interesting to try to understand why some of the MX$_4$ molecules form a plastic crystal while others do not. Detailed molecular dynamical calculation will be able to disclose the overall picture but we have discovered an interesting relation between the molecular shape and the crystal structure such as the one that exists among alkali halide crystals.

Table 1 shows values of the ratio of atomic radii[20] $r(\mathrm{M})/r(\mathrm{X})$. The dotted line across the Table separates the regions of the existence of a plastic phase. The limiting radius ratio below which the atom M can fit into the cavity formed by a close-packed tetrahedron of four X atoms is 0.23. Table 1 suggests that if the ratio is larger than 0.24, the molecule does not form a plastic crystal; it is presumably because the interaction between molecular octupoles, which is the lowest possible electric multipole for such a tetrahedral molecule,[21] is then so large that reorientation of molecules can not average the directional character of interaction. Carbon tetrafluoride is an exception to this rule but it is very close to the limiting case. It will be interesting to examine germanium iodide for existence of a plastic phase since it also lies close to the borderline.

References

1) B. Post, *Acta Crystallogr.*, **12**, 349 (1959).

2) F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56**, 413 (1972).

3) J. P. Badiali, J. Bruneaux-Poulle, and A. Defrain, *J. Chim. Phys.*, **73**, 113 (1976).

4) W. M. Latimer, *J. Am. Chem. Soc.*, **44**, 90 (1922).

5) H. H. Sisler, W. J. Wilson, B. J. Gibbins, H. H. Batey, B. Pfahler, and R. Mattair, *J. Am. Chem. Soc.*, **70**, 3818 (1948).

6) H. Kawaji, T. Atake, and H. Chihara, to be published.

7) R. Rudman and B. Post, *Science*, **154**, 1009 (1966).

8) S. Sengupta, G. Litzistorf, and E. A. C. Lucken, *J. Magn. Reson.*, **42**, 45 (1981).

9) J. Van Kranendonk and M. Walker, *Phys. Rev. Lett.*, **18**, 70 (1967).

10) S. Alexander and A. Tzalmona, *Phys. Rev.*, *A***138**, 845 (1965).

11) H. A. Rasing, *Mol. Cryst. Liq. Cryst.*, **9**, 101 (1969).

12) H. W. Spiess, R. Grosescu, and U. Haeberlen, *Chem. Phys.*, **6**, 226 (1974).

13) J. Virlet and P. Rigny, *Chem. Phys. Lett.*, **4**, 501 (1970).

14) H. Chihara and N. Nakamura, *Mol. Cryst. Liq. Cryst.*, **41**, (Letters), 21 (1977).

15) H. Chihara and Y. Koga, *Bull. Chem. Soc. Jpn.*, **44**, 2681 (1971).

16) V. P. Brand and H. Sackmann, *Z. Anorg. Allg. Chem.*, **321**, 262 (1963).

17) V. P. Brand and H. Sackmann, *Acta Crystallogr.*, **16**, 446 (1963).

18) D. Biedenkapp and A. Weiss, *Z. Naturforsch.*, **19a**, 1518 (1964).

19) A. L. Shawlow, *J. Chem. Phys.*, **22**, 1211 (1954).

20) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

21) H. M. James and T. A. Keeman, *J. Chem. Phys.*, **31**, 12 (1959).