NOTES

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Nuclear Spin-lattice Relaxation in $Sn(CH_3)_4$

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Synopsis. Nuclear magnetic relaxation T_1 of solid $Sn(CH_3)_4$ increased monotonously with temperature between 77 and 217 K. The activation energy for intramolecular methyl reorientation was 2.6 ± 0.3 kJ mol^{-1}. From measurements on the liquid phase, the apparent activation energy associated with the relaxation process was 8.6 kJ mol^{-1}. Differential thermal analyses revealed the existence of another unstable solid phase.

Tetramethylstannane $Sn(CH_3)_4$ was studied by nuclear magnetic resonance by Smith¹⁾ who measured the spin-lattice relaxation time T_1 by the method of signal decay. We have re-examined the solid and the liquid phases of $Sn(CH_3)_4$ by calorimetry and NMR. This Note will describe the NMR results and point out some new features which supplement the previous studies.

Differential Thermal Analyses

Unlike its lighter homologues $C(CH_3)_4$²⁾ and $Si(CH_3)_4$³⁾, $Sn(CH_3)_4$ has no plastic crystal phase below its triple point. However, differential thermal analyses revealed that an unstable solid phase appeared when the liquid is cooled through the freezing point. This unstable phase spontaneously transforms itself to the stable phase which has the melting point at 217 K. We were not able to hold the unstable phase long enough to make NMR measurements, and it was not made certain whether it was a plastic crystal phase.

NMR Line Width

The temperature dependence of the NMR line-width was measured on a polycrystalline specimen; the width remained constant at 5.7 ± 0.6 G from 20 K to the melting point**. Corresponding to this, the second moment was 9.0 ± 1.0 G^2, which roughly agrees with 8.4 G^2 calculated on the basis of fully excited intramolecular methyl reorientation. When measured with a specimen of poorer purity (99.8 moles per cent), a narrow absorption peak was super-imposed on a broad signal, which was also reported by Smith. However, a purer specimen*** (better than 99.99 moles per cent) did not show the narrow peak.

Spin-Lattice Relaxation Time

The spin-lattice relaxation time T_1 at 10 MHz was measured between 77 K and the melting point by $\pi/2$-τ-$\pi/2$ pulse sequences and between 182 K and 244 K (undercooled and normal liquid) by π-τ-$\pi/2$ pulses. The results are shown in Fig. 1. In the solid state, the T_1 values here obtained show a monotonous increase with temperature and are shorter than the values reported by Smith by a factor of 2: There is no trend of levelling off above 160 K either. On the assumption that we are looking at extreme narrowing case, $\omega\tau_c \ll 1$, which we believe plausible, the activation energy for intra-methyl reorientation was derived as 2.6 ± 0.3 kJ mol^{-1} in comparison with Smith's value¹⁾ 1.93 ± 0.05 kJ mol^{-1} and with Durig's value⁴⁾ 3.35 kJ mol^{-1} derived from far infrared study.

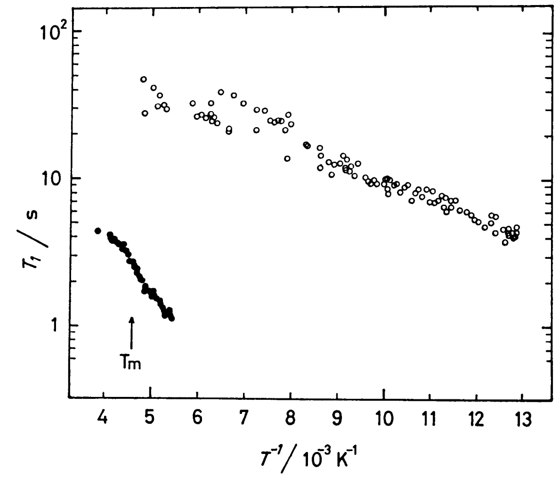

Fig. 1. A semilog plot of T_1 *vs.* the inverse temperature for $Sn(CH_3)_4$ as observed at 10 MHz.
(●) liquid phase, (○) crystal phase.

From the T_1 in the liquid state, an apparent activation energy was obtained as 8.6 ± 1.0 kJ mol^{-1}. It is interesting to note that this is close to the enthalpy of fusion⁵⁾ 9.24 ± 0.05 kJ mol^{-1}. It is difficult to assess the mode or modes of motion responsible for the relaxation in this temperature region, but it is likely that self-diffusion is at least partly responsible for that.

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References

1) G. W. Smith, *J. Chem. Phys.*, **42**, 4229 (1965).
2) J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.*, **58**, 2354 (1936).
3) T. Hasebe, G. Soda, and H. Chihara, *Proc. Jpn. Acad.*, **51**, 168 (1975).
4) J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.*, **52**, 2046 (1970).
5) T. Atake and H. Chihara, to be published.

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** 1 G = 10^{-4} T

*** Purification was carried out by a preparative gas chromatograph. The thermodynamic properties of this purer specimen will be reported elsewhere.⁵⁾