Rotational Excitations and Tunnelling of Non-Equivalent Methyl Groups in $Pb(CH_3)_4$

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Rotational tunnelling and librations of the methyl groups in tetramethyllead have been measured as a function of temperature by inelastic neutron scattering. Tunnel splittings of 74 µeV and 30.7 µeV and librational peaks at 3.6 meV and 10.2 meV have been observed. The data show that $Pb(CH_3)_4$ is isomorphous to $Sn(CH_3)_4$ with a space group Pa3, $Z = 8$ and the molecules at c-sites. Rotational potentials for both types of inequivalent CH_3 groups are derived and used for the explanation of NMR-T_1 measurements.

1. Introduction

Rotational tunnelling of CH_3 groups in solids has been studied extensively in recent years using most of all inelastic neutron scattering (INS) and nuclear magnetic resonance (NMR) techniques [1–3]. Various materials have been examined, and the number of tunnel splittings measured has been greatly augmented. In this way several rotational potentials could be determined.

In the tetramethylmetal compounds $X(CH_3)_4$ the tunnel frequency was found to increase greatly in the sequence of X=Si, Ge, Sn, and Pb. The systematic reduction of the strength of the rotational potential with increasing size of the molecule can be explained by a dominant intramolecular interaction with the neighbouring CH_3 groups in the same molecule, as discussed in [3]. While the results for X=Si, Ge, Sn could be interpreted consistently [3, 4], there were considerable problems in understanding the data of tetramethyllead (TML). TML represents a case where methyl group rotation is hindered only slightly, and is therefore especially interesting. In the NMR spin-lattice relaxation rate $1/T_1$, the peak which occurs at lower temperature is field dependent and a second and third one are not. In many cases, this behaviour can be explained in terms of tunnelling methyl groups whose tunnel frequencies in the torsional ground state ω_t^0 are much larger than the Lamor frequency ω_0 [5–7]. The apparent activation energy then changes from the real activation energy E_A to a lower value E_{01}, the energy difference between the first excited and librational ground state. Such an interpretation, for TML, leads to unreasonable parameters [3] and to a disagreement with the tunnel splitting observed earlier by INS [8]. We therefore concluded that there are most probably non-equivalent methyl groups as already found in tetramethyltin [4]. The aim of the present study is to obtain complete information on the rotational potentials of methyl groups in $Pb(CH_3)_4$ by measuring all energy transfers above 0.3 µeV by INS. A knowledge of the rotational excitations is not only necessary for understanding the structure and the methyl group tunnelling of TML, but also for the discussion of the behaviour of non-equivalent CH_3 groups and the interpretation of NMR-T_1 results.

2. Experimental Results and their Discussion

TML was obtained from the OCTEL company as a mixture of 50% TML–50% ethanol. After addition of water this mixture separates into a H_2O-ethanol and a TML-phase. The TML-phase is extracted and dried by adding a small amount of anhydrous sodium sulphate. The TML was filled into a flat sample container of Nb with dimensions $30 \times 30 \times 1\ mm^3$. This sample was used in all experiments.

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The neutron scattering of samples containing hydrogen is dominated by the large incoherent scattering cross section of the protons. Thus the spectra of TML mainly show the excitations of the methyl group, i.e. tunnelling, librations and phonons involving the protons at low temperatures, and quasielastic scattering due to classical jump reorientation at higher temperatures. In this paper we concentrate on the low temperature regime. Measurements were done with three types of spectrometers, the backscattering instrument IN 10 and the cold time of flight (TOF) spectrometer IN 5 at the ILL Grenoble [9], and the thermal TOF machine SV 22 in Jülich [10]. Thus the full range of energy transfers from 0.3 µeV to 20 meV was covered.

A rough estimate of the number of CH_3 groups participating in molecular reorientation and the corresponding potentials can be obtained with a socalled "fixed-window" scan, which measures the elastic intensity within the energy resolution of the spectrometer ("energy window") as a function of temperature. Figure 1 shows the result of such an experiment as measured with the IN 10 with an energy resolution $\delta E_{\mathrm{res}} = 1.2\ \mu\mathrm{eV}$ at a momentum transfer $Q = 1.8\ \text{Å}^{-1}$. The intensity drops in a narrow temperature interval at a very low temperature to a new stable level. Hereafter it decreases slowly up to the melting temperature T_{m} where it falls to a background level in a sharp step. This step shows a hysteresis due to undercooling of the sample. There is no indication of a second soft step just below T_{m}. This is in contradiction to an earlier measurement, where such a step was found and interpreted as the onset of a rotation of the whole molecule [8]. Three quantities of this curve can be evaluated with respect to molecular rotation: the temperature $T_{1/2} = 13\ \mathrm{K}$ corresponding to the intensity at half height of the step, the height of the step relative to the intensity at $T = 0\ \mathrm{K}$, and the slope of the curve. The step in the intensity has the following reason: Due to the onset of jump reorientation some elastic scattering becomes quasielastic. With increasing temperature an increasing amount of this quasielastic scattering is outside the range of the elastic window. The jump rate follows an Arrhenius-law

$$\nu_{\mathrm{c}} = \nu_0 \exp\left(-E_{\mathrm{A}}/kT\right) . \tag{1}$$

Experience shows that the prefactor changes very little for CH_3 groups in different rotational potentials and is $\nu_0 \approx 10^{12}\ \mathrm{s}^{-1}$. Because of the results from the tunnelling spectra (see below) we use here $\nu_0 = 2 \cdot 10^{12}\ \mathrm{s}^{-1}$. The linewidth of the quasielastic line in neutron scattering is related to the jump rate via

$$\Gamma(T) = \tfrac{3}{2} h\, \nu_{\mathrm{c}} = \Gamma_0 \exp\left(-E_{\mathrm{A}}/kT\right) . \tag{2}$$

Because of $\Gamma = \delta E_{\mathrm{res}}$ at $T_{1/2}$, we can estimate

$$E_{\mathrm{a}} = \ln\left(\frac{\Gamma_0}{\delta E_{\mathrm{res}}}\right) T_{1/2} . \tag{3}$$

A step at low $T_{1/2}$ thus corresponds to a weak rotational potential. From (3) we estimate $E_{\mathrm{A}}/k \approx 100\ \mathrm{K}$ in TML.

The slow drop of the intensity over the whole range of temperature can be described by a Debye-Waller factor (DWF) $\exp\left(-Q^2 \langle u^2 \rangle\right)$. The dominant contribution to the displccement u is due to the libration of the CH_3 groups. In shallow potentials u is large and the librational states are close to each other. Thus a step at low temperature is always accompanied with a large slope. In principle, the mean square displacement at low temperatures can be derived which is related to the width of the ground-state wavefunction. For a more detailed discussion see [11].

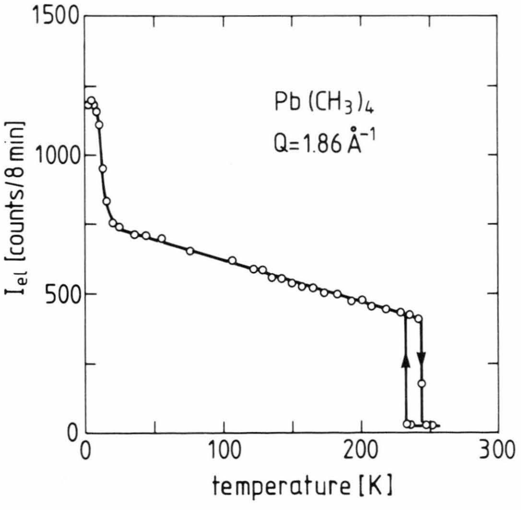

Fig. 1. Temperature dependence of the elastic incoherent intensity measured with the backscattering spectrometer IN 10 of the ILL Grenoble. The energy resolution was $\delta E = 1.2\ \mu\mathrm{eV}$ at a momentum transfer $Q = 1.80\ \text{Å}^{-1}$ (fixed window measurement). The step at low temperature shows the onset of methyl reorientation, that at high temperature the melting of the sample.

To understand the height of the drop in the intensity ΔI at $T_{1/2}$ with $\Delta I/I = 0.39$ we have to discuss the scattering law of *one* tunnelling methyl group in a polycrystal [1, 12]

$$\begin{aligned} S(Q,\omega) &= [1+2j_0(Qd)]\,\delta(\omega) + \tfrac{2}{3}[1-j_0(Qd)] \\ &\quad \cdot [L(\Gamma,-\omega_t) + L(\Gamma,+\omega_t) + L(\Gamma,0)] \\ &= I_{el}\,\delta(\omega) + I_{inel}\,[L(\Gamma,-\omega_t) \\ &\quad + L(\Gamma,+\omega_t) + L(\Gamma,0)] \end{aligned} \tag{4}$$

with the Lorentzian $L(\Gamma,\omega_i) = \dfrac{1}{\pi}\,\dfrac{\Gamma}{\Gamma^2 + (\omega-\omega_i)^2}$ describing the tunnelling lines at energy transfer $\hbar\omega_t$, and a quasielastic contribution at $\hbar\omega = 0$. j_0 is a spherical Bessel function, Q the momentum transfer to the sample in the scattering experiment, and $d = 1.78$ Å is the distance between two protons in the CH_3-group. We have to distinguish between two cases:

i) The tunnelling lines are not resolved by the spectrometer ($\hbar\omega_t \ll \delta E_{res}$).

In this case the step has a height

$$\frac{\Delta I}{I} = \frac{3I_{inel}}{I_{el} + 3I_{inel}} = \frac{2}{3}(1-j_0) = 0.68$$

for the experimental value of $Q = 1.8$ Å^{-1} (the argument of j_0 has been omitted for simplicity).

ii) The tunnelling lines are well resolved ($\hbar\omega_t \gg \delta E_{res}$). In this case the intensity at low temperatures is already reduced and for the experimental $Q = 1.8$ Å^{-1}

$$\frac{\Delta I}{I} = \frac{I_{inel}}{I_{el} + I_{inel}} = \frac{2(1-j_0)}{5+4j_0} = 0.41\ .$$

Thus the step is smaller for case i) than for case ii). If there are inequivalent CH_3 groups in a compound the above considerations have to be applied to these groups individually and $\Delta I/I$ then is the result of the weighted average. The experimental result for TML clearly shows that all tunnel transitions are at energies larger than the resolution of the IN 10 spectrometer.

The data of a second detector at $Q = 1.3$ Å^{-1} are consistent with the above conclusions.

Tunnelling spectra of TML were recorded with two instruments. With the IN 10 the energy range below 38 μeV was investigated. While no tunnelling transition was found between 0.2 μeV and 14 μeV using the standard set-up of the spectrometer with an unpolished Si[111] monochromator crystal and $\delta E_{res} = 1.2$ μeV, the transition already known [8] was detected at $\hbar\omega_t^0(1) = 30.7$ μeV using the offset configuration with the CaF_2[111] monochromator crystal and $\delta E_{res} = 1.2$ μeV. Figure 2 shows three spectra taken at the indicated sample temperatures. The shift and broadening of this transition was evaluated in the temperature range $1.6\ \mathrm{K} < T < 18.6\ \mathrm{K}$ and are shown in Figure 3. The line shifts a little to larger energies in contrast to theoretical expectations [13] and many other experimental results [1, 3, 4, 7] which show a decrease of the splitting with temperature. The broadening is considerable and follows an Arrhenius law (Fig. 3) with an activation energy $E_\Gamma \approx 9$ meV and a prefactor $\Gamma_0 = 2$ meV. According to Hewson [13] E_Γ should be similar to E_{01}, which is the energy of the first excited librational state.

The investigated energy range has been extended to the energy of the free rotor using the high resolution TOF spectrometer IN 5 with an incoming wavelength $\lambda_0 = 10.17$ Å and a energy resolution $\delta E_{res} = 18$ μeV. The detectors were arranged around a momentum transfer $Q = 1.13$ Å^{-1}. The spectrum measured at low temperature $T = 1.6$ K is shown in the relevant energy range in Figure 4. Besides the

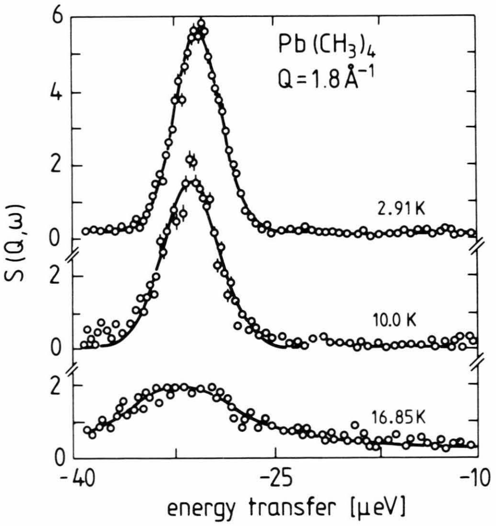

Fig. 2. Tunnelling spectra of TML as measured at the indicated temperatures with IN 10 in the offset configuration covering the energy range $10\ \mu\mathrm{eV} < E < 38\ \mu\mathrm{eV}$ with an energy resolution $\delta E_{res} = 1.2$ μeV at $Q = 1.8$ Å^{-1}.

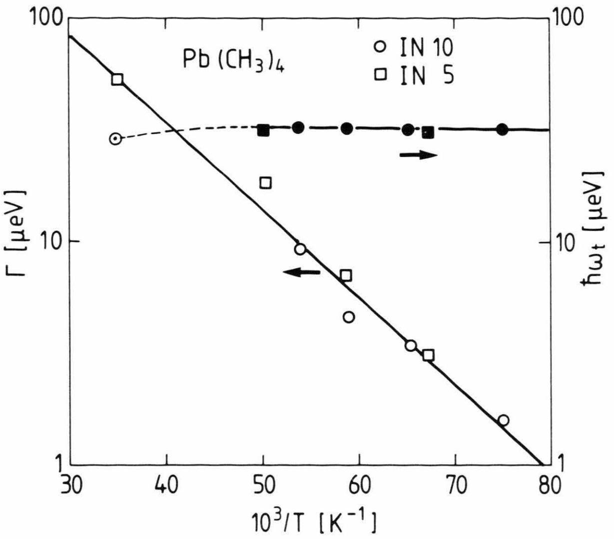

Fig. 3. Temperature dependence of the tunnelling splitting with $\hbar\omega_t^0 = 30.7\,\mu eV$ (● IN 10, ■ IN 5, ⊙ NMR) and Arrhenius plot of its width (○ IN 10, □ IN 5). The data are taken from the measurements of Figs. 2 and 4.

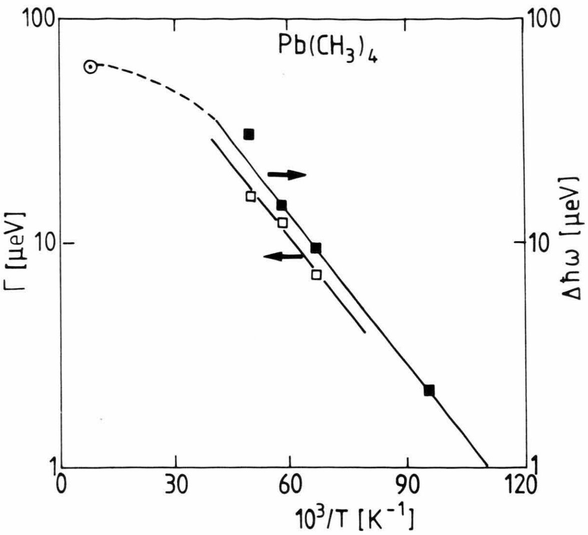

Fig. 5. Arrhenius plot of the shift and the width of the tunnelling line at $\hbar\omega_t^0 = 74\,\mu eV$. Symbols as Figure 3.

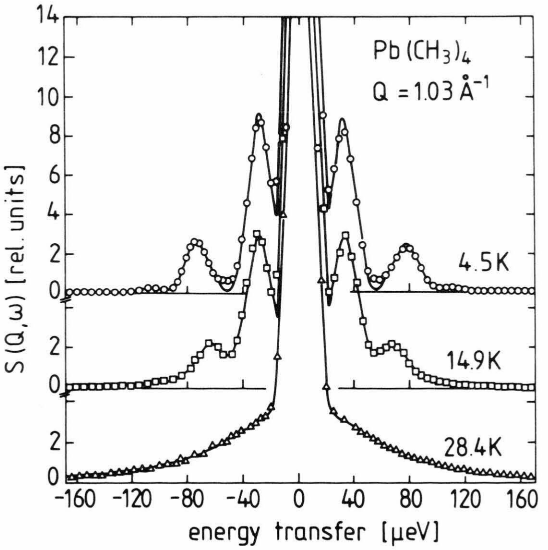

Fig. 4. Tunnelling spectra of TML as measured at the temperatures indicated, and $Q = 1.13\,Å^{-1}$ with IN 5 using an incoming wavelength $\lambda_0 = 10.17\,Å$ and a corresponding energy resolution $\delta E = 18\,\mu eV$.

already known tunnelling transition at 30.7 μeV a further transition is observed at $\hbar\omega_t^0(2) = 74\,\mu eV$. Its intensity is about 1/3 of that of the inner tunnelling line. Following exactly the arguments of [4] and supported by the fixed-window scan, we conclude on the basis of the scattering law (4):

i) From the total elastic and inelastic intensities, it may be deduced that there are no further tunnelling lines.

ii) The intensity ratio 3 : 1 of the tunnelling lines is the consequence of a threefold axis at the molecular site, which makes one CH_3 group different from the three others. The analogy to $Sn(CH_3)_4$ suggests also in this case the space group Pa3 [14].

iii) The weaker tunnelling line occurs at higher energy. This finding is opposite to the situation in $Sn(CH_3)_4$. If the rotational potentials of both types of CH_3 groups would show a similar shape this would mean that in TML molecule is elongated along the threefold axis. For a discussion of this point see Section 5.

The temperature dependence of the spectra measured with IN 5 was also evaluated. The values of the linewidth for the transition $\hbar\omega_t^0(1)$ are plotted in addition to the results from IN 10 in Figure 3. The results are consistent, but the IN 5 values systematically lie somewhat below the IN 10 data, which are more accurate. The outer tunnelling line $\hbar\omega_t^0(2)$ could by analyzed accurately enough only in a narrow temperature range before it overlaps with the inner line. The shift and broadening with temperature correspond to the theory and are shown in Figure 5. The activation energies extracted from an Arrhenius fit are rather low and nearly equal for the shift and the width: $E_\Gamma \approx E_S \approx 3$ meV. This seems to be reasonable since there is no peak in the density of states below 4 meV [13]. The prefactor $\Gamma_0 = 0.25$ meV is astonishingly small, however. At a temperature $T = 28.4$ K the spectrum looks already quasielastic (cf. Figure 4).

The density of states of TML was measured with the thermal TOF spectrometer SV 22 at the medium flux research reactor FRJ2 in Jülich [10]. An incoming wavelength $\lambda_0 = 2.02$ Å was used which gave an energy resolution $\delta E = 1.04$ meV covering an energy range $E < 15$ meV. The spectrum after subtracting the background and converting into $S(Q, \omega)$ is shown in Figure 6. Since TML is a rather soft material the low temperature of $T = 8$ K was necessary to obtain well-defined sharp peaks. The energies corresponding to the peaks are 3.6, 4.5, 6.5, 9.0, 10.2 and 12.2 meV. The spectrum is very sensitive to temperature augmentation. At $T = 14$ K the lines are already considerably broadened. The most intense lines in the spectrum are due to the nearly dispersionless librations or zone boundary phonons. From the temperature dependence of both the width of the tunnelling lines and the damping of the peaks in the density of states [7] we conclude that the peaks at energies $E = 3.6$ meV and ~ 9.6 meV are librational peaks. The near-by peaks may eventually reveal the tunnel splitting of the first excited librational state. The assignment is, however, not unambiguous.

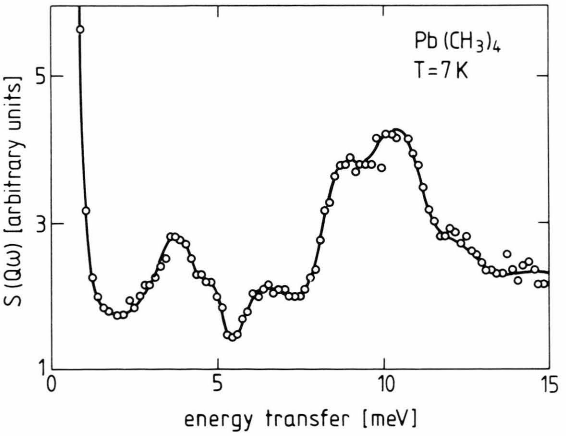

Fig. 6. Density of states of Pb(CH$_3$)$_4$ as measured with the thermal TOF spectrometer SV 22 using a wavelength $\lambda_0 = 2.02$ Å and $\delta E_{\text{res}} = 1.04$ meV in a range $2\,\text{Å}^{-1} < Q < 5\,\text{Å}^{-1}$.

3. Rotational Potential

Similar to previous papers [3, 4, 7, 15] we describe the rotational potential by the first two terms of the Fourier expansion with the basic threefold symmetry of the methyl group

$$V(\varphi) = \tfrac{1}{2} V_3 [1 + (-1)^k \cos 3\varphi] + \tfrac{1}{2} V_6 [1 + (-1)^k \cos 6\varphi]\,. \tag{5}$$

Tabulated eigenvalues of the Schrödinger equation for the one-dimensional methyl rotator are available with this potential. In order to determine the parameters V_3, V_6 and k from the experimental groundstate tunnel splittings $\hbar\omega_t^0(1) = 30.7\,\mu$eV, $\hbar\omega_t^0(2) = 74\,\mu$eV and the librational excitations (cf. Fig. 6) $E_{01}(1) = 9.6$ meV, $E_{01}(2) = 3.6$ meV, we plotted in Fig. 7 the curves of constant $\hbar\omega_t^0$ and E_{01} in a diagram $V_s = V_3 + V_6$ versus $\delta = V_3/V_s$ using the solutions of the Schrödinger equation. Both CH$_3$ rotors are considered to be independent.

As can be seen from Fig. 7 for each rotor there are two solutions which are listed in Table 1. Since the shape of the potential in most earlier experiments, did not deviate significantly from threefold symmetry [2, 3], we favour the solutions a) and c).

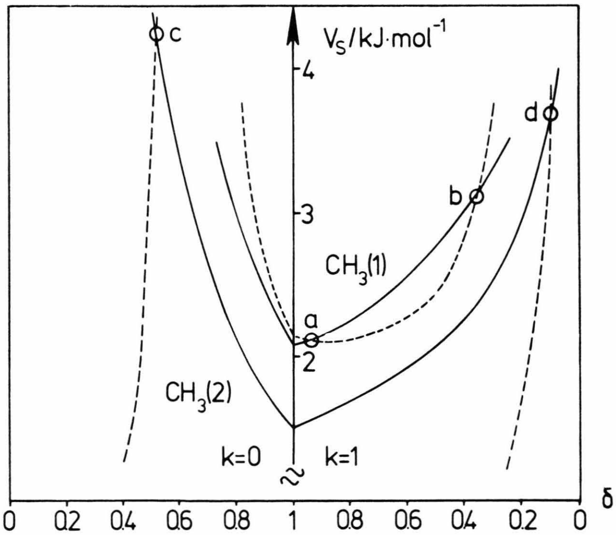

Fig. 7. Lines of constant tunnel splitting (——) and lines of constant librational energy E_{01} (---) for both types of methyl groups in the parameter space of the potential of Eq. (5) $V_S = V_3 + V_6$ vs. $\delta = V_3/V_S$. The labelled intersections of the curves define the rotational potentials tabulated in Table 1.

Table 1. Potential parameters as obtained from the measured groundstate tunnel splitting $\hbar\omega_t^0$ and the first excited librational energy E_{01} for both inequivalent methyl groups in TML.

	Solution	$\hbar\omega_t^0$ / μeV	E_{01} / meV	V_S / kJ/mol	δ	k	E_A / kJ/mol
CH_3 (1)	a	30.7	9.6	2.1	0.95	1	1.5
	b			3.0	0.38	1	1.6
CH_3 (2)	c	74	3.6	4.3	0.52	0	2.7
	d			3.7	0.10	1	2.3

While the more abundant CH_3 (1) rotors with solution a) obviously behave similar to the results obtained for $Si(CH_3)_4$, $Ge(CH_3)_4$ and $Sn(CH_3)_4$ (1) with nearly threefold potentials and $k = 1$ [3], the CH_3 (2) rotor is hindered by a potential which contains an important sixfold contribution. In the same way as in $Sn(CH_3)_4$, the total barrier height and the activation energy are larger for the CH_3 (2) group, but because of the sixfold term tunnelling occurs at higher frequency. The particular shape of the potential with alternating high and small barriers may lead to rotational jumps in the classical regime which are either governed by the activation energy $E_A(\varphi = 0°) = 2.7$ kJ/mol or by $E_A(\varphi = 60°) = E_A(\varphi = 0°) - V_3 = 0.5$ kJ/mol. The classical jump reorientation in such a potential is treated in a separate paper [16]. The result of $E_A \approx 0.83$ kJ/mol obtained from the quasielastic fixed-window scan may be interpreted in terms of a superposition of $E_A(1) = 1.5$ kJ/mol and $E_A(2) = 0.5$ kJ/mol, and the latter value is also supposed to govern the relaxation.

4. Spin-Lattice Relaxation Rates

In principle, the experimental NMR data [3] can be fitted by Haupt's model [6], which yields for polycrystalline materials, on the assumption that $\omega_t \gg \omega_0$

$$\frac{1}{T_1} = 4C_{AE}\frac{\tau_c}{1+\omega_t^2\tau_c^2} + C_{EE}\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right]. \tag{6}$$

The first term in Eq. (6) accounts for relaxation by intramolecular magnetic dipole interaction within a CH_3 group which is always connected with a rotator transition from A to E symmetry. The theoretical value of the relaxation strength is $C_{AE}/(p\,\delta^2) = 4 \cdot 10^9\ s^{-2}$, where p denotes the ratio of methyl protons causing relaxation over the total number of protons, and δ^2 is an efficiency factor which is supposed to be slightly less than one. The second term in (6) occurs as a result of interactions with protons other than those producing relaxation.

Equation (6) was successfully applied to several systems, and various information such as activation energies or the temperature dependence of tunnel splittings and correlation times could be extracted from the data. In many cases the approximation

$$\frac{1}{\tau_c} = \frac{1}{\tau_0'}\exp(-E_A'/RT) + \frac{1}{\tau_0''}\exp(-E_A''/RT) \tag{7}$$

was used for the correlation time $\tau_c = 1/\nu_c$, where the limiting values $E_A' \approx E_A$ and $E_A'' \approx E_{01}$ were often obtained in agreement with neutron scattering data [4, 15].

In the case of TML, the fit of the experimental points by using (6) and (7) resulted in unreasonable parameters [3]. The apparent activation energies E_A' and E_A'' did not show clear correlation with the INS data and the pre-exponentials τ_0' and τ_0'' appeared too large compared with other methyl rotators.

Considering the results of the present study, however, the reason for this discrepancy is obvious. NMR delivers only global information on the motion, which describes the details well if the methyl groups are all equal. If there are non-equivalent CH_3 groups, however, as already observed in $Sn(CH_3)_4$, the effect of both kinds of rotators and the mutual coupling has to be taken into account. Such an attempt is made in Fig. 8.

Each rotor is described separately by (6) and (7) and the superposition gives the experimental curve. The CH_3 (1) rotor is governed by $E_A' = 1.5$ kJ/mol and $E_A'' = 0.93$ kJ/mol, and CH_3 (2) by 0.5 kJ/mol (cf. section no. 3) and 0.25 kJ/mol, respectively. Figure 8 shows that the $1/T_1$ maximum due to intramolecular interaction at $10^3/T = 35\ K^{-1}$ is rather large as expected, and leads to a tunnel energy of $\hbar\omega_t \approx 29$ μeV, which agrees well with the neutron data of Figure 3. On the other hand, the relaxation rate assigned to the rotors CH_3 (2) has a relatively more important intermolecular contribution; the small intramolecular maximum near $10^3/T = 10$ corresponds to a tunnel energy of about 9 μeV, which is compatible with the strong tem-

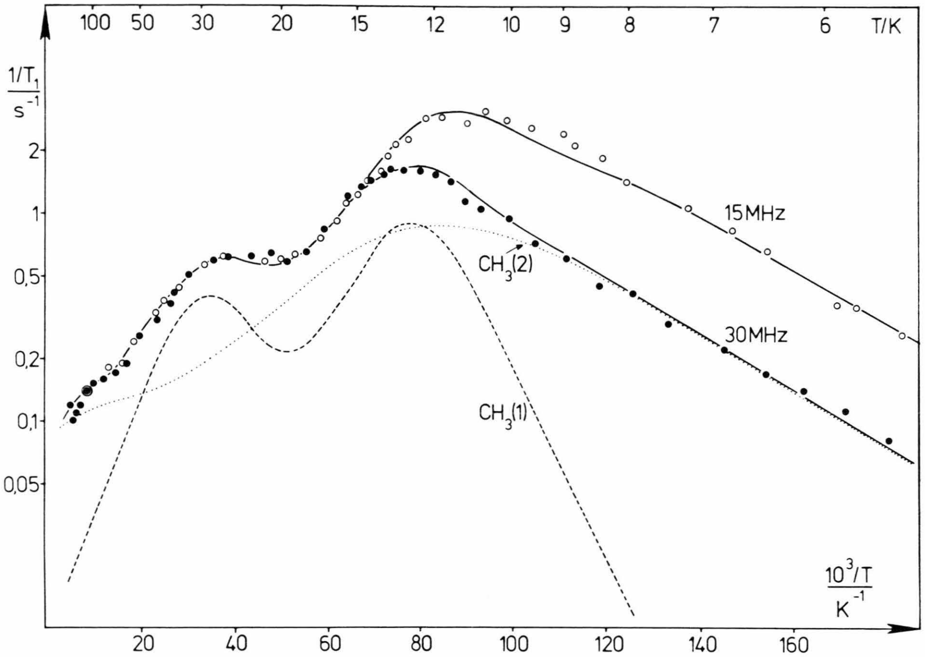

Fig. 8. Interpretation of the experimental NMR spin-lattice relaxation rate of TML in terms of a superpositions of two non-equivalent methyl rotators CH$_3$ (1) (–––) and CH$_3$ (2) (·····) as explained in the text.

perature dependence of this tunnel line in Figure 5. It is not clear why E''_A (2) is smaller than E_{01} (2) measured by INS.

5. Conclusion

Tunnelling and reorientation of methyl groups in solids is difficult to be analyzed when non-equivalent CH$_3$ rotors are present. The most complete information is obtained from INS if all rotational excitations are actually detected. The temperature dependence of tunnelling transitions plays the most important role in finding the correct assignment of tunnelling and librational excitations. Interpretation of the more global data delivered by NMR relaxation is not unambiguous without detailed knowledge of the system. In the present example of Tb(CH$_3$)$_4$, the situation is in many ways similar to that observed previously in Sn(CH$_3$)$_4$. The structure of the tunnelling spectra is the same. Thus a space group Pa3 is assumed also for TML. In both cases the CH$_3$ (2) group in the molecule which is different from the other three is hindered by a higher rotational barrier showing that the molecule is compressed along the threefold axis. In Pb(CH$_3$)$_4$, however, there is an important sixfold contribution which makes the groundstate tunnel splitting larger. On the other hand, upon elevation of temperature the smaller ground state tunnelling frequency changes only slightly while the larger one decreases drastically.

Thus the two inequivalent methyl groups have a very different temperature dependence, though they are imbedded in the same phonon spectrum. In our opinion this situation seems to provide a good basis for a better theoretical understanding of the temperature dependence of rotational tunnelling.

Acknowledgement

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