Eine theoretisch interessante Möglichkeit zur Beeinflussung der Gemischtrennung bietet auch die in Gl. (19) und (20) wegen der Annahme  $T={\rm const}$  nicht berücksichtigte Thermodiffusion. Wegen des in weiten Bereichen der Trenndüse von der Umlenkwand nach innen gerichteten Temperaturgefälles <sup>13</sup> dürfte sie im Prinzip zu einer Verminderung der UF<sub>6</sub>-Sedimentation führen. Da eine entsprechende, gegen den Zentrifugaleffekt gerichtete Thermodiffusion der Isotope wahrscheinlich zu vernachlässigen

ist <sup>14</sup>, könnte die Thermodiffusion über das leichte Zusatzgas auf indirektem Wege zur Entmischung der Uranisotope beitragen.

Abschließend sei noch darauf hingewiesen, daß in der Trenndüse wegen der Kombination von großer Mach-Zahl und großer Knudsen-Zahl ein merklicher Einfluß gaskinetischer Effekte höherer Ordnung zu erwarten ist. Rechnungen nach dem Momentenverfahren haben gezeigt, daß sich daraus meßbare Beiträge zur Isotopentrennung ergeben können.

einigen 10<sup>-5</sup>. Nach Untersuchungen von S. K. Deb und A. K. Barua (Phys. Fluids 10, 992 [1967]) ist mit keiner wesentlichen Veränderung des Thermodiffusionsfaktors durch das leichte Zusatzgas zu rechnen.

# <sup>73</sup>Ge Nuclear Magnetic Resonance Studies

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The  $^{73}\mathrm{Ge}$  spectra of some germanium-tetra-halides, germanium-tetra-alkyles, and of germanium-tetra-methoxide have been observed. The chemical shifts of these  $^{73}\mathrm{Ge}$  NMR-lines were measured as functions of the temperature in the range up to 50 °C. In CS2- and benzene-solutions of GeI4, two  $^{73}\mathrm{Ge}$ -lines were found. The  $^{73}\mathrm{Ge}$  NMR-spectrum of Ge(CH3)4 caused by indirect spin-spin-coupling between the  $^{73}\mathrm{Ge}$  nucleus and the protons is well resolved. The spin-spin-coupling constants of Ge(CH3)4 and of Ge(OCH3)4, which shows an unresolved spectrum, were evaluated by an iterative least square fitting routine. The relaxation times  $T_2$  (in the range  $30\ldots740$  msec) measured by the Carr-Purcell spin-echo-technique and calculated from the line widths are in good agreement. Precision measurements of the ratios of the Larmor frequencies of  $^{73}\mathrm{Ge}$  in GeCl4,  $^{41}\mathrm{K}$  in aqueous KF-solution and  $^{2}\mathrm{H}$  in pure heavy water lead to a magnetic moment of  $^{73}\mathrm{Ge}$ :  $\mu=-(0.876\,78\pm0.000\,01)~\mu_{\mathrm{N}}$  (uncorrected).

## 1. Introduction

The  $^{73}$ Ge nucleus (natural abundance 7.6%, and Larmor frequency 2.7 MHz in a field  $B_0 \approx 18 \text{ kG}$ ) delivers a weak NMR-signal; it is about 6 orders of magnitude weaker than the NMR-signal of protons in  $H_2O$  in the same magnetic field  $B_0$ , and with the same probe volume. There are only three  $^{73}$ Ge NMR-studies  $^{1-3}$  on  $GeCl_4$ , but no high resolution ones on other compounds.

<sup>73</sup>Ge has a nuclear spin <sup>4</sup> I = 9/2 and an electrical quadrupole moment Q = -0.29 barn <sup>5</sup>. Therefore

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<sup>1</sup> C. D. Jeffries, Phys. Rev. 92, 1262 [1953].

one expects broad resonance lines of molecules with unspherical symmetry, i. e. a rapid decay of the NMR-signals; e. g. the NMR-signal of methyl-germanium-trichloride decays so rapidly that we were not able to find it. This yields an upper limit for the relaxation time  $T_2 < 100~\mu{\rm sec}$ .

On the other hand, narrow NMR-lines are expected from germanium compounds with spherical symmetry. As there exist some NMR-investigations of tetrahedral compounds of the Group IV-elements e. g. <sup>13</sup>C, <sup>29</sup>Si, and <sup>119</sup>Sn, we investigated such germanium compounds.

- <sup>3</sup> O. Lutz, A. Schwenk, and G. Zimmermann, Phys. Letters 25 A, 653 [1967].
- J. M. Mays and C. H. Townes, Phys. Rev. 81, 940 [1951].
   W. J. Childs and L. S. Goodman, Phys. Rev. 141, 15 [1966].



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<sup>&</sup>lt;sup>13</sup> U. Ehrfeld, Interner Bericht des Instituts für Kernverfahrenstechnik KVT 55/25 [1970].

Nach Messungen von P. Kirch und R. Schütte (Z. Naturforsch. 22 a, 1532 [1967]) liegt der Thermodiffusionsfaktor von gasförmigem UF<sub>6</sub> nur in der Größenordnung von

<sup>&</sup>lt;sup>2</sup> S. I. AKSENOV and K. V. VLADMIRSKII, Dokl. Akad. Nauk SSSR 96, 37 [1954].

Although there would be some interest to investigate mixed Ge-halides, as this was done by Burke and Lauterbur 6 with tin(IV)-halides, it is not worth while with the <sup>73</sup>Ge resonance, as the line widths of unsymmetrical compounds are larger than the chemical shifts of these lines in usual fields  $B_0$ .

### 2. Experimental

### 2.1. Apparatus

The apparatus, developped to detect very weak NMR-signals, is a pulsed spectrometer described in  $^{7,8}$ . The magnetic field  $B_0=18.07$  kG is stabilized with a  $^7$ Li-NMR-probe  $^9$ . The spatial homogeneity is achieved by special nickel-shims. The probe assembly, with a one-coil-arrangement, permits a sample rotation up to 270 Hz. By a thermostat the temperature of the sample is to be held constant within an accuracy of  $\pm 1$   $^{\circ}$ C.

A resolution of  $2\cdot 10^{-7}$  is obtained with this probe assembly and with a sample volume of 1.5 cm³, i. e. at the  $^{73}$ Ge resonance frequency of 2.7 MHz the width of a NMR-line caused by the inhomogeneity is less than 0.4 Hz, on the other hand, relaxation times  $T_2 \approx 200$  msec can be determined from the free-precession decay of the NMR-signal with an influence less than 10% due to the inhomogeneity of the magnetic field.

The measurements were done in such a manner that the NMR-signal decays completely during the time interval (0.1...2 sec) between the rf-pulses. The signal/noise-ratio was improved by using a time-averaging-computer (Signal Analyzer 5480 A of Hewlett Packard).

## 2.2. Evaluation of the NMR-signals

The signal stored in the time-averaging-computer is transferred to a computer (CDC 3300 of the ZDV, Tübingen) by punched tape to calculate the Fourier-Transform of the averaged data. The real part of this Fourier-Transform, the absorption spectrum is a Lorentzian line with a half width:

$$\Delta \nu_{1/2} = 1/(\pi T_2)$$
 (1)

in the case of an exponentially decaying free-precession-signal,  $T_2$  is the transverse relaxation time.

Shifts were measured by the sample replacement method. The evaluation of the Carr-Purcell spin-echos was done by Fourier-Transformation of each echo, i.e. of the NMR-signal between two successive  $180^{\circ}$ -pulses respectively. Time intervals between the  $180^{\circ}$ -pulses were chosen in such a way, that the decay of the NMR-signal due to the magnetic field inhomogeneity was small. The maximum of the absolute value of the Fourier-Transform of an echo is proportional to the height of this echo. From the decay of these maxima  $T_2$  is calculated.

The determination of absolute values of spin-spin-coupling constants was done by an iterative least square fitting routine. The number of lines in a spectrum and their relative intensities are well known; under this assumption, the following parameters of the spectrum can be calculated by this routine: the centre of the line group, the coupling constant, the width of a single line, and the absolute intensity of the lines.

### 2.3. Samples

The samples were all contained in cylindrical glass tubes of 9 mm internal diameter, and most were measured at a temperature of  $(30\pm1)\,^{\circ}\text{C}.$  At this temperature all of them, with the exception of GeI<sub>4</sub> were liquids. GeBr<sub>4</sub> which melts at 26  $^{\circ}\text{C}$  was undercooled for measurements at deeper temperatures.

The GeI<sub>4</sub> samples were a 2.3-molar solution in CS<sub>2</sub> and a 0.57-molar solution in benzene. These concentrations correspond nearly with the saturated solutions at a temperature of 40  $^{\circ} C$  which was the measuring temperature of the two GeI<sub>4</sub> samples.

GeCl<sub>4</sub> and tetra-methyl-germane (GeMe<sub>4</sub>) were delivered by the Schuchardt GmbH, München. GeBr<sub>4</sub>, GeI<sub>4</sub>, tetra-ethyl-germane (GeEt<sub>4</sub>), tetra-propyl-germane (GePro<sub>4</sub>), tetra-butyl-germane (GeBu<sub>4</sub>), and Ge(OCH<sub>3</sub>)<sub>4</sub> were manufactured by the Alfa Inorganic, Inc., Beverly. The purities of the germanium-halides are 99.999%, those of the organometallic compounds are in the range 97...99.9%.

#### 3. Results

# 3.1. The Ratio of the Larmor Frequencies of <sup>73</sup>Ge, <sup>41</sup>K, and <sup>2</sup>H

Our former measurements of the Larmor frequency  $^3$  of  $^{73}$ Ge were carried out with a pulse period T, small compared with the relaxation time  $T_2$ . This pulse technique, described in  $^8$  as "Fall 3", avoids signal loss due to the inhomogeneity of the field  $B_0$ , the NMR-lines are broadened by saturation, but in an inhomogeneous field  $B_0$  shifts between the maximum of such a line and the Larmor frequency may occur  $^{10}$ . This effect was underestimated at that time. Now we were able to repeat those measurements with a smaller and rotating probe sample, the pulse period  $T \approx 1$  sec was now longer than the relaxation times  $T_1$  and  $T_2$ , therefore such errors are eliminated.

The Larmor frequencies of <sup>73</sup>Ge, and <sup>41</sup>K were measured with the pulse spectrometer. The Larmor

<sup>8</sup> A. Schwenk, Z. Phys. **213**, 482 [1968].

<sup>10</sup> A. Schwenk, J. Magn. Resonance, in press.

<sup>&</sup>lt;sup>6</sup> J. J. Burke and P. C. Lauterbur, J. Amer. Chem. Soc. 83, 326 [1961].

<sup>&</sup>lt;sup>7</sup> J. KAUFMANN and A. SCHWENK, Phys. Letters 24 A, 115 [1967].

<sup>&</sup>lt;sup>9</sup> J. KAUFMANN and A. SCHWENK, Z. Angew. Phys. 21, 527 [1966].

frequency of <sup>2</sup>H was detected with a normal crossedcoil NMR-spectrometer \*. The samples were GeCl<sub>4</sub>, a 9-molar aqueous solution of KF and pure heavy water.

From about 40 measurements with each probe, the following results, corrected for spherical probe shape, are obtained:

$$\begin{array}{l} \nu^{\rm rs}_{\rm Ge}/\nu^{\rm rt}_{\rm K} = 1.361\ 966\ 4\pm0.000\ 000\ 5\ . \\ \nu^{\rm rs}_{\rm Ge}/\nu^{\rm r}_{\rm H} = 0.227\ 248\ 6\pm0.000\ 001\ 0\ , \\ \nu^{\rm rt}_{\rm K}/\nu^{\rm r}_{\rm H} = 0.166\ 853\ 1\pm0.000\ 000\ 8\ . \end{array}$$

The errors of the second and the third result are the sum of the following errors: three times the r.m.s. error, an error of  $\pm 2$  ppm, caused by the different field distributions across the two samples and an error of  $\pm 2$  ppm, which arises from the uncertainty in the magnetic field value within the two different probe assemblies. The error of the first result is three times the r.m.s. error, as both Larmor frequencies were determined with the same probe assembly. With the third and the first results one gets

$$v^{78}_{\mathrm{Ge}}/v^{2}_{\mathrm{H}} = 0.227\ 248\ 3\ \pm 0.000\ 001\ 0$$

which is in good agreement with the value of the second result.

Using the nuclear spin of  $^{73}$ Ge, I=9/2, the ratio  $\nu_{^{2}\mathrm{H}}/\nu_{^{1}\mathrm{H}}$  of Smaller  $^{11}$ , and the proton moment (uncorrected for  $\mathrm{H_{2}O}$ ) of Cohen and DuMond  $^{12}$ , and the sign detected by Jeffries  $^{1}$ , one gets the magnetic moment of  $^{73}$ Ge in GeCl<sub>4</sub> without corrections:

$$\mu^{78}_{\mathrm{Ge}} = - \, (0.876\,78 \pm 0.000\,01) \,\,\mu_{\mathrm{N}} \,.$$

### 3.2. Chemical Shifts

The <sup>73</sup>Ge chemical shifts were measured in the tetra-halides and some organometallic compounds. The results are given in Table 1. The chemical shift is defined:

$$\delta_x = (\nu_{\mathrm{ref}} - \nu_x) / \nu_{\mathrm{ref}}$$

(both frequencies measured at the same field  $B_{\mathbf{0}}$ ).

All of the shifts are reported as parts per million (ppm), relative to the resonance frequency of the reference GeCl<sub>4</sub>. The values are corrected to spherical probe-shape, except that of Ge(OCH<sub>3</sub>)<sub>4</sub>, the corrections are less than 0.5 ppm. The error is three times the r.m.s. error.

In both solutions of  $GeI_4$ , there are two lines of the  $^{73}Ge$  resonance with the intensity ratio  $\approx 4:1$ . The stronger line is due to the molecule  $GeI_4$ , whereas the weaker line could be due to a chain compound of the type  $I_3Ge-GeI_3$  or to  $GeI_2$ . This assumption is based on the fact that free iodine was pointed out in both solutions.

Table 1. 73Ge chemical shifts of germanium-tetra-compounds.

Compound	Solvent	Chemical shift/ppm	Remarks
GeCl <sub>4</sub>	_	0	reference
GeBr <sub>4</sub>		$343.0 \pm 0.3$	_
$GeI_4$	benzene	$1139.0 \pm 0.5$	stronger line
	benzene	$852 \pm 3$	weaker line
$GeI_4$	$CS_2$	$1111.6 \pm 0.5$	stronger line
_	$CS_2$	$831 \pm 5$	weaker line
$Ge(OCH_3)_4$	-	$66.9 \pm 0.2$	_
$GeMe_4$		$30.9 \pm 0.5$	
$GeEt_4$		$12.8 \pm 0.2$	
$GePro_4$	-	$28.8 \pm 0.3$	_
$GeBu_4$		$25.4 \pm 0.3$	_

### 3.3. Temperature Dependence of Chemical Shifts

All compounds mentioned above, except GeMe $_4$ , and GeI $_4$ , were investigated for a temperature dependence of the chemical shift of the <sup>73</sup>Ge resonance. Within the limits of error, neither the chemical shift of all germanium-alkyles in the range  $20\ldots40$  °C, nor the shift of GeCl $_4$  in the range  $0\ldots50$  °C depend on the temperature. A dependence of the chemical shift on the temperature  $\Theta$  was found at GeBr $_4$  and Ge(OCH $_3$ ) $_4$ . The shifts are to be described by the following functions:

$$\begin{split} \delta(\Theta) = 341.1 \text{ ppm} + (0.059 \text{ ppm/}^{\circ}\text{C}) \cdot \Theta \\ \text{for GeBr}_4 \text{ in the range } 20 \,^{\circ}\text{C} \leq \Theta \leq 40 \,^{\circ}\text{C} \\ \text{and } \delta(\Theta) = 66.2 \text{ ppm} + (0.026 \text{ ppm/}^{\circ}\text{C}) \cdot \Theta \\ \text{for Ge(OCH}_3)_4 \text{ in the range } 0 \,^{\circ}\text{C} \leq \Theta \leq 50 \,^{\circ}\text{C}. \end{split}$$
 The error is maximum  $\pm 0.2 \text{ ppm}.$ 

<sup>13</sup>C, <sup>29</sup>Si, and <sup>119</sup>Sn-chemical shifts of the alkyles and halides were measured by Hunter and Ree-

<sup>\*</sup> We like to thank Dr. O. Lutz for performing the <sup>2</sup>H mea-

<sup>&</sup>lt;sup>11</sup> B. SMALLER, Phys. Rev. 83, 812 [1951].

<sup>&</sup>lt;sup>12</sup> E. R. COHEN and J. W. DUMOND, Rev. Mod. Phys. **37**, 537 [1965].

VES <sup>13</sup>, LAUTERBUR <sup>14, 15</sup>, and BURKE and LAUTERBUR <sup>6</sup>. Figure 1 shows the shifts of the alkyles as measured till now. In Fig. 2, the shifts of the halides are plotted. The shifts of all elements in both figures, are related to the tetra-chloride as reference. The chemical shifts between the various germanium-

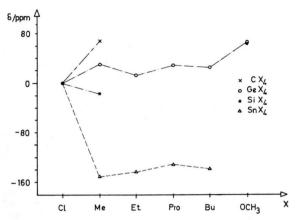


Fig. 1. Chemical shifts of some tetra-alkyles of the Group IVelements <sup>29</sup>Si, <sup>73</sup>Ge, and <sup>119</sup>Sn related to the tetra-chloride. The <sup>29</sup>Si-measurements were performed by Hunter and Reeves <sup>13</sup>, and those of <sup>119</sup>Sn by Burke and Lauterbur <sup>6</sup>, and Hunter and Reeves <sup>13</sup>.

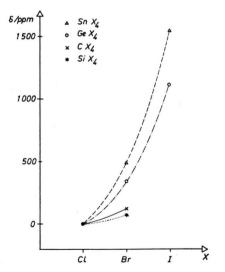


Fig. 2. Chemical shifts of the tetra-halides of the Group IV-elements <sup>13</sup>C, <sup>29</sup>Si, <sup>73</sup>Ge, and <sup>119</sup>Sn related to the tetra-chloride. The <sup>13</sup>C-measurements were performed by Lauterbur <sup>14</sup>, those of <sup>29</sup>Si by Lauterbur <sup>15</sup> and Hunter and Reeves <sup>13</sup>, and those of <sup>119</sup>Sn by Burke and Lauterbur <sup>6</sup>.

alkyles are relatively small just as the shifts of the other alkyles yet measured. In relation to the  $GeCl_4$ , the germanium alkyles show a slightly positive shift, whereas the resonances of the tin-alkyles are more than  $130~\rm ppm$  negatively shifted in relation to the  $SnCl_4$  resonance. The shifts of the tetra-halides of the elements mentioned above show a similar trend; e. g. between the chemical shifts of the tin-halides  $\delta_{SnX_4}$  and those of the germanium-halides, the following relation holds:

$$\delta_{\mathrm{SnX}} = 1.41 \, \delta_{\mathrm{GeX}}$$
 (X = Br, I).

## 3.5. Indirect Spin-Spin-Coupling Constants

The protons in the alkyl-groups of the organometallic Ge-compounds are coupled to the  $^{73}$ Ge nucleus by indirect spin-spin-coupling. Figure 3 shows the  $^{73}$ Ge NMR-spectrum of Ge(CH<sub>3</sub>)<sub>4</sub>.

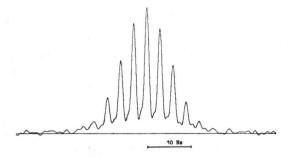


Fig. 3. 73Ge NMR-spectrum of Ge(CH<sub>3</sub>)<sub>4</sub>.

As all protons are equivalent spins, this spectrum consists of 13 lines with the intensities proportional to the binomial coefficients  $\binom{12}{k}$ ,  $(k=0,\ldots,12)$ . 9 of these lines are to be seen in this spectrum, the other ones are less than the noise. From 12 such spectra, the absolute value of the coupling constant was evaluated by the fitting routine:

$$J_{^{73}\text{Ge}^{-1}\text{H}} = (2.99 \pm 0.03) \text{ Hz for Ge(CH}_3)_4$$
.

The error is the maximum error.

This coupling constant has also been determined in 1963 by SMITH <sup>16</sup>, and in 1964 by SZALMONA <sup>17</sup> from the proton NMR-spectrum of GeMe<sub>4</sub>. The results are:

$$J = (2.92 \pm 0.02) \text{ Hz}$$
 (Smith),  
 $J = 2.94$  Hz (Szalmona).

<sup>&</sup>lt;sup>13</sup> B. K. HUNTER and L. W. REEVES, Can. J. Chem. 46, 1399 [1968].

<sup>&</sup>lt;sup>14</sup> P. C. LAUTERBUR, J. Chem. Phys. 26, 217 [1957].

P. C. LAUTERBUR, in: Determination of Organic Structures by Physical Methods, edit. by F. C. NACHOD and W. D. PHILLIPS, Academic Press, New York 1962, Vol. 2.

<sup>&</sup>lt;sup>16</sup> G. W. Smith, J. Chem. Phys. 39, 2031 [1963].

<sup>&</sup>lt;sup>17</sup> A. SZALMONA, Molec. Phys. 7, 497 [1964].

A similar case as described here is found at germanium-tetra-methoxide Ge(OCH<sub>3</sub>)<sub>4</sub>; this compound should also deliver a NMR-spectrum of 13 lines. The absorption curve of Ge(OCH<sub>3</sub>)<sub>4</sub> is essentially different from a Lorentzian shape as recorded at all Ge-halides; this leads to the supposition of an unresolved spectrum. Indeed, the least square fitting routine delivers besides the absolute value of the coupling constant of Ge(OCH<sub>3</sub>)<sub>4</sub>

$$J_{^{73}\text{Ge}} = {}^{1}\text{H} = (1.9 \pm 0.3) \text{ Hz}$$

the half width of a single line  $\Delta\nu_{1/2} = (12.2 \pm 1.5) \, \text{Hz}$ , which is in good agreement with the relaxation time  $T_2 = (30 \pm 3)$  msec measured by the Carr-Purcell method (see Sect. 3.7).

The other germanium alkyles investigated here, have not only one kind of equivalent protons; a more complicated structure of the NMR-spectrum results from this. The recorded absorption-curves show only one NMR-line, which differs strongly from a Lorentzian shape i. e. there is an unresolved spectrum; the half width of the NMR-line is  $3\dots 7$  times greater than the width of a single NMR-line calculated from the relaxation time  $T_2$ , as measured by the Carr-Purcell spin-echo technique (Sect. 3.7).

Because of the complicated structure of these spectra, we were not able to evaluate coupling constants by the least-square fitting routine.

### 3.6. Line Widths

To evaluate the relaxation time  $T_2$  from the width of a NMR-line, a very homogeneous field  $B_0$  is necessary, particularly if there are narrow NMR-lines.

By the rotation of the probe, field gradients perpendicular to the axis of rotation are eliminated; the line widths are only influenced by an inhomogeneity parallel to this axis. The <sup>7</sup>Li-probe <sup>9</sup>, which is used to measure and to stabilize the field  $B_0$ , can also be used to measure the inhomogeneity. By a good adjustment of the nickel-shims, a variation of  $B_0$  in the range of the probe sample  $\Delta B/B_0 \approx 10^{-7}$  can be achieved.

The influence on the line width of a constant field gradient parallel to the direction of the field  $B_0$  has been calculated by DOLEGA <sup>18</sup>. According to this result, the measured line widths, which are not too much influenced by the inhomogeneity of  $B_0$ , can be corrected to get the natural line widths, as they would

be recorded in an absolutely homogeneous field. In Table 2, the line widths are given with these corrections, and also the relaxation times  $T_2$  calculated with the aid of Eq. (1).

Germanium methoxide  $Ge(OCH_3)_4$  shows a significant dependence of the line width on the temperature  $\Theta$ :

$$\Delta v_{1/2} = 22.2 \text{ Hz} - (0.16 \text{ Hz}/^{\circ}\text{C}) \cdot \Theta$$

in the range 0  $\leq$   $\Theta$   $\leq$  50 °C. The error is maximum  $\pm\,0.7\,\mathrm{Hz}.$ 

In the range 20...40 °C the line widths of the germanium-tetra-alkyles did not show a dependence on the temperature within the limits of error.

Table 2. Line widths, relaxation times  $T_2$  calculated from line widths and measured by the Carr-Purcell spin-echo method. The measurements were performed at a temperature  $\Theta = 40$  °C for GeI<sub>4</sub> and at  $\Theta = 30$  °C for the other compounds. The errors of the line widths and the related  $T_2$  values are three times the r.m.s. error plus a systematical error of  $\pm 0.04$  Hz due to the uncertainty of the inhomogeneity-correction and due to the fluctuations of  $B_0$  in time. The errors of the Carr-Purcell results are the maximum errors.

Compound	Line With $\triangle v_{1/2}/\mathrm{Hz}$	$T_2/\mathrm{msec}$ from the line width	$T_2/\text{msec}$ measured by the Carr-Purcell spinecho-techn.
GeCl <sub>4</sub> GeBr <sub>4</sub>	$2.02 \pm 0.10 \\ 1.76 + 0.14$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$163 \pm 20 \\ 196 + 30$
$GeI_4a$	$2.2 \ \pm 0.3$	$145  \stackrel{-}{\pm} 23$	$190 \pm 30$
$GeI_4$ a, b $Ge(OCH_3)_4$	$\frac{32}{17.7} + 0.8  ^{\mathrm{c}}$	$\frac{10}{(18.0 + 0.9)}$	
$Ge(OCH_3)_4$	$12.2~\pm1.5$ d	$26 \pm 3$	$\frac{30 \pm 3}{240 \pm 80}$
$\begin{array}{c} \mathrm{GeMe_4} \\ \mathrm{GeEt_4} \end{array}$	$egin{array}{c} 0.58 \pm 0.16 \ 15.6 \ \pm 0.4 \ ^{ m c} \end{array}$	$\begin{array}{c} 550 & \pm 200 \\ (20.4 \pm 0.5) \end{array}$	$740 \pm 80 \ 140 \pm 20$
$GePro_4$ $GeBu_4$	$egin{array}{ccc} 13.3 & \pm 0.2\ {}^{ m c} \\ 13.8 & + 0.5\ {}^{ m c} \end{array}$	$(23.9 \pm 0.4)$ (23.1 + 0.8)	$rac{100 \pm 12}{65 + 7}$

a The NMR-line widths of GeI<sub>4</sub> in CS<sub>2</sub> and benzene are the same.

## 3.7. Relaxation Times T<sub>2</sub>

The relaxation times  $T_2$  of germanium compounds were also determined by the spin-echo technique of Carr and Purcell <sup>19</sup>. The inhomogeneity of the rf-field  $B_1$  in the range of the probe sample, causes different precession angles during the rf-irradiation at different points of the sample. This effect, intensified by the  $B_0$ -inhomogeneity, would cause a decrease of the echos after successive pulses even with-

b Weaker line.

c Width of the absorption curve of the unresolved spectrum.

d Width of the single line calculated with the fitting routine.

<sup>&</sup>lt;sup>18</sup> U. Dolega, Ann. Phys. **16**, 153 [1955].

out transverse relaxation. This decrease was calculated <sup>20</sup>, and the measured values were corrected.

All measurements were performed at a temperature of the sample of 30 °C; the results are given in column 4 of Table 2; the errors are the maximum errors.

Comparing the  $T_2$  values attained by the spin-echo technique of Carr and Purcell with those calculated from the line widths, there is agreement within the limits of error with  $\operatorname{GeCl}_4$ ,  $\operatorname{GeBr}_4$ , and  $\operatorname{GeMe}_4$ . The

<sup>20</sup> W. Sahm, Diplomarbeit, Tübingen 1970.

relaxation time  $T_2$  of  $\mathrm{Ge}(\mathrm{OCH_3})_4$ , measured by the Carr-Purcell technique, corresponds to that calculated for a single line by the least square fitting routine. The relaxation times of the other germanium alkyles do not correspond with the widths of the NMR-lines, as these lines consist in an unresolved spectrum of many single NMR-lines.

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## Estimating the Alpha-Particles Transmission through a Barrier

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Among the numerous doubts associated with the estimation of the alpha-decay penetrabilities, two queries have been selected in order to investigate their justification: is the ambiguous determination of  $\alpha$ -nucleus potential a real obstacle and is the JWKB an inadequate approximation?

In the study of alpha decay, theoretical successes have been invariably achieved only in reproducing the general features of experimental data, i. e. in explaining behaviours but not absolute values. Thus the first great accomplishment was the explanation of the marked dependence of the halflife upon the energy of the emitted  $\alpha$ -particle as due to the energy dependence of the penetrability factor <sup>1, 2</sup> and the second was the explanation of the reduced widths varying with the mass number as due to the variation of the  $\alpha$ -particle formation probability with the level assignments of the most loosely bound four nucleons <sup>3</sup>.

As for absolute values, no approach has given a satisfactory explanation, and every time the authors, in their conclusions, nurtured the hope that the discrepancy recorded was largely due to some insufficiencies in the determination of the penetrabilities. The impossibility of unequivocal determination of the a-nucleus potential, the inaccuracy of the first-

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<sup>1</sup> G. Gamov, Z. Physik 51, 204 [1928].

 U. E. CONDON and R. W. GURNEY, Nature London 122, 439 [1928].

<sup>3</sup> H. J. Mang, Phys. Rev. 119, 1069 [1960].

<sup>4</sup> H. J. Mang, Ann. Rev. Nucl. Sci. 14, 1 [1964].

order JWKB approximation, the nonlocality of the potential barrier, the uncertainties in assessing the decay energies, the neglect or approximate consideration of the coupling between different possible channels, are only some of the numerous insufficiencies invoked <sup>4-8</sup>.

The first two have been taken up in this letter in order to establish if these can really be held responsible for the said discrepancy, of some orders of magnitude, existing between the theoretical and the experimental absolute values of the decay constant. For this purpose we have applied the theoretical considerations briefly reviewed below to the ground-ground state transitions in even-even polonium isotopes.

Alpha-decay constant has long been considered  $^9$  to be a product of the probability of  $\alpha$ -particle formation inside the nucleus and the probability of where  $R_{\rm in}$  and  $R_{\rm out}$  are the internal and outer turning points given by Q(r)=0.

<sup>5</sup> GY. BENCZE and A. SANDULESCU, Physics Letters 22, 473 [1966].

<sup>6</sup> Gy. Bencze, Physics Letters 23, 713 [1967].

<sup>7</sup> E. A. RAUSCHER, J. O. RASMUSSEN, and K. HARADA, Nucl. Phys. A **94**, 33 [1967].

J. K. POGGENBURG, H. J. MANG, and J. O. RASMUSSEN, Phys. Rev. 181, 1967 [1969].

<sup>9</sup> R. G. THOMAS, Progr. Theoret. Phys., Kyoto 12, 253 [1954] and the references quoted there.