^{127}I, ^{185}Re and ^{187}Re Solid State NMR Measurements on $(CH_3)_4AsIO_4$ and $(CH_3)_4AsReO_4$

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Tetramethylarsonium-metaperiodate shows ^{127}I solid state NMR signals without any visible quadrupole splitting. Due to the very large nuclear quadrupole moments of the rhenium isotopes ^{185,187}Re, the analogous Re compound exhibits the expected second order quadrupole NMR effects. The measured ^{185,187}Re NMR powder spectra contain superimposed signals arising from two different types of ReO_4^- tetrahedra, indicating that part of the ReO_4^- anions deviate only slightly from tetrahedral symmetry, while the other part are nearly undistorted ReO_4^- anions.

The temperature dependence of the solid state NMR spectra reveals phase transitions for both compounds, which are confirmed also by DSC analyses. Furthermore, the DSC analysis of the Re compound again proves the existence of the two different types of ReO_4^- tetrahedra in the lattice of the high temperature modification.

1. Introduction

Several different kinds of ^{127}I solid state NMR spectra of metaperiodates with alkyl-substituted cations of main group V have been found so far. The spectra manifest second order quadrupole interactions with quadrupole coupling constants in the range of 2−15 MHz at room temperature [1−3].

In the ^{127}I solid state NMR spectra of tetraethyl-ammonium- and tetramethylphosphonium-meta-periodate, resolved first or second order quadrupole effects cannot be detected [4]. Compared to the ^{127}I-nucleus, with a nuclear quadrupole moment Q = −0.7 barn, the ^{185}Re and ^{187}Re isotopes possess extremely large nuclear quadrupole moments Q(^{185}Re) = 2.8 barn and Q(^{187}Re) = 2.6 barn. Therefore we calculated the maximum values of the quadrupole coupling constants for the isomorphous metaperrhenates [4]. On measuring the ^{185}Re and ^{187}Re solid state NMR spectra of the corresponding compounds, we observed a different behaviour. No quadrupole interactions are visible in the ^{185}Re and ^{187}Re powder NMR spectra of $(C_2H_5)_4NReO_4$. By contrast, the ^{185}Re and ^{187}Re NMR spectra of $(CH_3)_4PReO_4$ show the expected quadrupole interaction with quadrupole coupling constants in the calculated range of 20 MHz at room temperature.

The present paper describes for the first time ^{127}I, ^{185}Re and ^{187}Re solid state NMR spectra of tetra-methylarsonium-metaperiodate (**1**) and the analogous metaperrhenate (**2**). The quadrupole disturbed line shapes of the ^{185}Re and ^{187}Re spectra are of high complexity and will be discussed in terms of second order quadrupole splitting. From the temperature dependence of the quadrupole interaction the very small deviations $\Delta\beta$ from tetrahedral symmetry of the ReO_4^- anions are calculated. Moreover, we observed phase transitions for both compounds. The phase transitions are discussed on the basis of NMR and DSC investigations.

2. Experimental

2.1. Instrumentation

The ^{127}I, ^{185}Re and ^{187}Re powder spectra were obtained with a Bruker FT-NMR CXP 200 spectrometer equipped with a superconducting magnet (B_0 = 4.698 T). Temperature dependent experiments were carried out using a Bruker B-VT 1000 thermostat with a temperature tolerance $\Delta T = \pm 1$ K. Experimental errors of the reported quadrupole coupling constants are in the order of $\Delta e^2qQ/h = \pm 0.2$ MHz.

The DSC measurements were done with a Perkin Elmer differential scanning calorimeter Model DSC-2 [5].

2.2. Preparation of the compounds (**1**) and (**2**)

The starting compound trimethylarsine was synthesized following the procedure of Zingaro and Merijanian [6]. Addition of methyliodide gave the quaternary arsonium salt [7]. The hydroxide $(CH_3)_4AsOH$ was synthesized by application of a

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strongly basic anion exchanger (Merck, Exchanger III). Neutralization of the basic solution with the equivalent amount of pure periodic acid gave the desired metaperiodate (**1**). The metaperrhenate (**2**) was prepared analogously by using an aqueous solution of perrhenic acid. This acid was obtained from $KReO_4$ using a strong acid cation exchanger (Merck, Exchanger I).

Recrystallization from water/ethanol gave analytically pure compounds. The data of the elemental analyses are as follows:

$C_4H_{12}AsIO_4$ (**1**)
Calcd   C 14.74   H 3.71   As 22.99   O 19.63   I 38.93,
Found   C 14.73   H 3.76   As 22.94   O 19.49   I 38.72.

$C_4H_{12}AsReO_4$ (**2**)
Calcd   C 12.47   H 3.14   As 19.45   O 16.61   Re 48.33,
Found   C 12.37   H 3.01   As 19.21   O 16.61   Re 48.74.

3. Results

3.1. ^{127}I Solid state NMR spectra of $(CH_3)_4AsIO_4$ (1)

For the first time polycrystalline $(CH_3)_4AsIO_4$ (**1**) was studied by ^{127}I solid state NMR spectroscopy. The temperature dependent spectra are shown in Fig. 1.

On lowering the temperature compound **1** shows chemical shift effects. The temperature dependent results are summarized in Table I and Fig. 2.
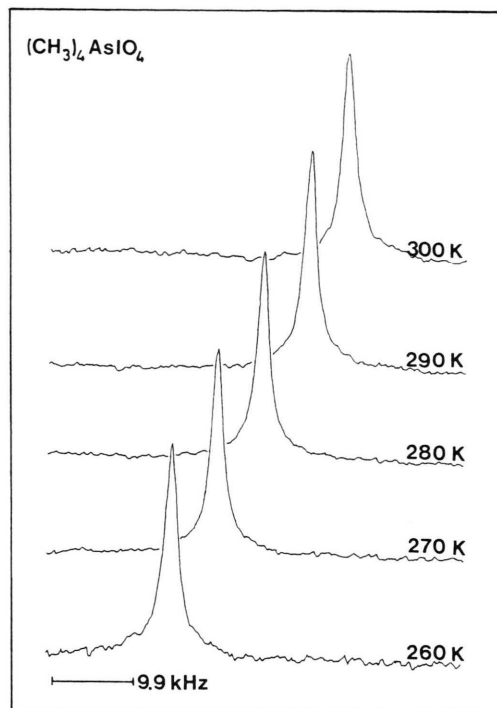

Fig. 1. ^{127}I solid state NMR spectra of polycrystalline $(CH_3)_4AsIO_4$ (**1**). Larmor frequency: $\nu_L = 40.19$ MHz; sweep range: SW = 100 kHz; pulse program: one cycle pulses; pulse width: DL1 = 5 μs; recycle time: DL0 = 40 ms; number of scans: NS = 50,000.
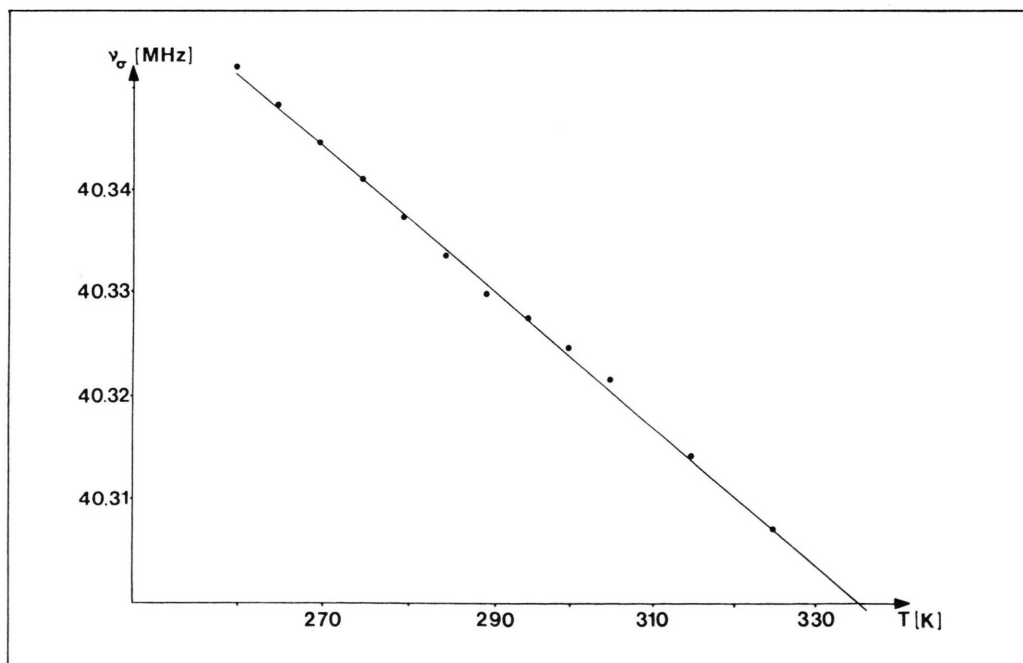

Fig. 2. Temperature dependent frequencies, ν_σ, of the ^{127}I NMR powder spectra of $(CH_3)_4AsIO_4$; the spectra are depicted in Fig. 1; the values of ν_σ from Table I.

T [K]	ν_σ [MHz]
335	40.300
325	40.307
315	40.314
305	40.322
300	40.325
295	40.328
290	40.330
285	40.334
280	40.337
275	40.341
270	40.345
265	40.348
260	40.352

Table I. Temperature dependent frequencies, ν_σ, of the ^{127}I NMR powder spectra of $(CH_3)_4AsIO_4$; the spectra are depicted in Fig. 1.

The line width of the dipolar broadened ^{127}I NMR resonance amounts to 2.5 kHz. This value is independent on temperature. At temperatures below 260 K, ^{127}I solid state NMR measurements of **1** give no signals. The DSC analysis shows a single peak for both temperature rise and temperature down measurements. This indicates a first order phase transition of **1** at T = 254(3) K (s. Fig. 3) [8, 9].

3.2. ^{185}Re and ^{187}Re Solid state NMR spectra of $(CH_3)_4AsReO_4$

In agreement with our calculations [4], ^{185}Re and ^{187}Re solid state NMR spectra of compound **2** could be detected. Fig. 4 shows the powder pattern obtained at T = 380 K with $NaReO_4$ in aqueous solution as a reference.

The natural abundance of the rhenium nuclei (^{185}Re: 37.1%, ^{187}Re: 62.9%) and the difference in the Larmor frequencies, ν_L ($\nu_L(^{185}Re)$ = 45.028 MHz, $\nu_L(^{187}Re)$ = 45.489 MHz), are very advantageous as the two isotopes can be observed simultaneously in the NMR spectra. The left part of the spectrum (at high frequency) shows ^{187}Re quadrupole splitting $\Delta\nu_{T=380\,K}$ = 22.5 kHz ± 1 kHz manifested by the outward frequency edges.

The quadrupole splitting of the ^{185}Re nucleus is larger ($\Delta\nu_{T=380\,K}$ = 25.4 kHz ± 1 kHz) as a consequence of the larger quadrupole moment of this Re isotope ($Q(^{185}Re)$ = 2.8 barn, $Q(^{187}Re)$ = 2.6 barn). Moreover, the distance between these two resonance signals is exactly equal to the difference in the Larmor frequencies of ^{185}Re and ^{187}Re.
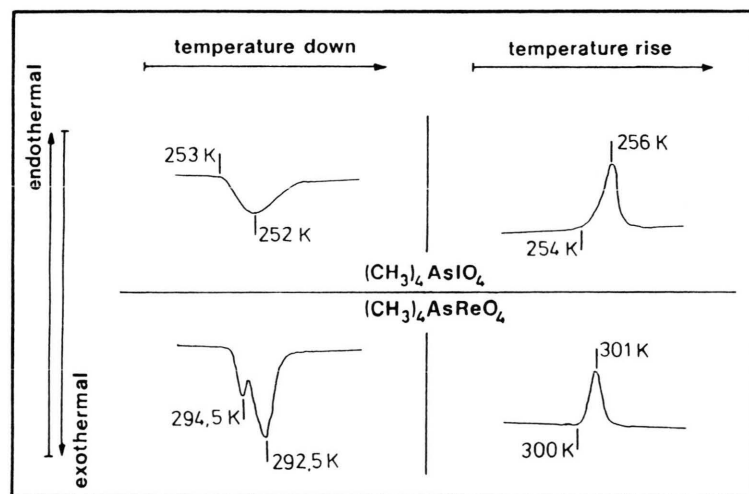

Fig. 3. DSC analysis of $(CH_3)_4AsIO_4$ and $(CH_3)_4AsReO_4$. The curves show a reversible first order phase transition for both compounds.
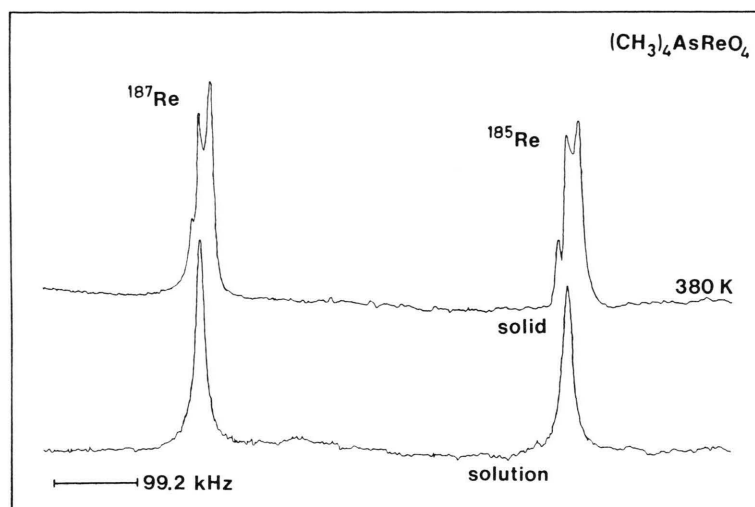
Fig. 4. [185]Re−[187]Re solid state NMR spectrum of $(CH_3)_4AsReO_4$ at T = 380 K with aqueous $NaReO_4$ solution as standard. Larmor frequency: ν_L = 45.25 MHz; sweep range: SW = 1 MHz; pulse program: one cycle pulses; pulse width: DL 1 = 5 μs; recycle time: DL0 = 40 ms; number of scans: NS = 30,000.

The temperature dependent [187]Re solid state NMR spectra of **2** are depicted in Fig. 5.

The [185, 187]Re powder spectra of **2** have additional signals arising from two different types of ReO_4^- tetrahedra in the lattice. The frequency edges B arise from a second order quadrupole splitting $\Delta\nu$ of the central [185, 187]Re NMR transition (m = +1/2 ↔ m = −1/2) associated with an axialsymmetric asymmetry parameter $\eta \approx 0$. The quadrupole coupling constants can be determined by applying equation (1).

$$e^2qQ/h = 4\sqrt{2}\ \sqrt{\Delta\nu\ \nu_L} \qquad (1)$$

with ν_L: Larmor frequency
$\Delta\nu$: quadrupole splitting

The temperature dependence of the data is summarized in Table II and Fig. 6.

In the temperature range of T < 310 K no [185]Re or [187]Re NMR signal can be achieved. The DSC analysis proves a reversible first order phase transition at T =

T [K]	$\Delta\nu$ [kHz]	e^2qQ/h [MHz]
380	22.32	5.70
370	23.37	5.83
360	25.81	6.13
350	31.04	6.72
340	39.06	7.54
330	53.01	8.79
320	68.71	10.00
310	92.77	11.62

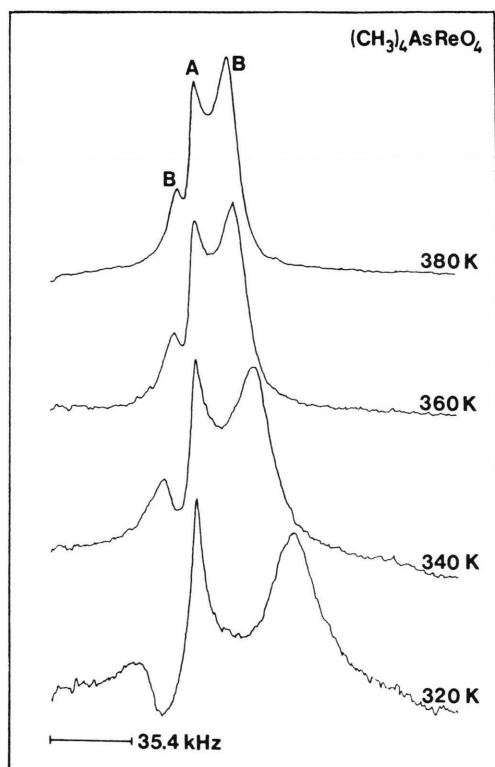Table II. Temperature dependence of second order [187]Re NMR quadrupole interactions of $(CH_3)_4AsReO_4$.

Fig. 5. Temperature dependence of the [187]Re solid state NMR spectra of polycrystalline $(CH_3)_4AsReO_4$. Larmor frequency: ν_L = 45.455 MHz; sweep width: SW = 357.1 kHz; pulse program: one cycle pulses; pulse width: DL 1 = 5 μs; recycle time: DL0 = 40 ms; number of scans: NS = 100,000. The average temperature coefficient is given by $\bar{\alpha} = \{2/[e^2qQ/h(T_1) + e^2qQ/h(T_2)]\} \cdot \{[e^2qQ/h(T_2) - e^2qQ/h(T_1)]/[T_2−T_1]\}$.
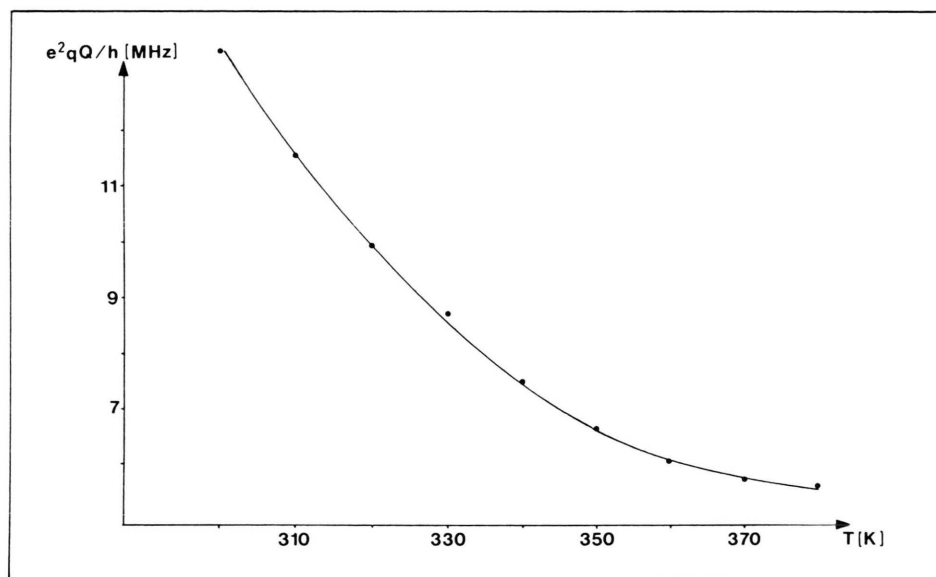
Fig. 6. Temperature dependence of ^{187}Re quadrupole coupling constants e^2qQ/h measured by second order quadrupole effects in ^{187}Re powder spectra of $(CH_3)_4AsReO_4$; values from Table II.

294 K for temperature down measurement and at T = 301 K for temperature rise measurement (s. Fig. 3).

4. Discussion

4.1. ^{127}I Solid state NMR spectra of $(CH_3)_4AsIO_4$ (1)

The ^{127}I powder spectra of **1** (s. Fig. 1) show the typical line shape for cases where dipolar coupling is the dominant solid state interaction in the lattice [10]. The presence of a very small quadrupole interaction hidden due to dipolar line broadening cannot be excluded.

From the line width the maximum value of the quadrupole coupling constant can be approximated to $e^2qQ/h \leq 1.8$ MHz. The iodine atoms must possess a nearly spherical electric environment, as provided by nearly undistorted IO_4^- tetrahedra. These results suggested that the analogous rhenium compound **2** should be suitable for NMR measurements.

4.2. ^{185}Re and ^{187}Re Solid state NMR spectra of $(CH_3)_4AsReO_4$

The ^{185}Re and ^{187}Re solid state NMR spectra of **2** (s. Fig. 4 and 5) show the characteristic features of a superposition of two different NMR resonances. This unusual line shape is a consequence of two dif-

ferent ReO_4^- tetrahedra in the lattice. We could observe comparable spectra in the ^{127}I solid state NMR spectra of tetraphenylarsonium-metaperiodate in a low temperature modification at $T \leq 205$ K [11, 12].

The DSC analysis gives another hint at the existence of two different types of ReO_4^- tetrahedra in the high temperature modification of **2**. The temperature down measured DSC spectra (s. Fig. 3) unequivocally show two distinguishable maxima caused by the different loss of energy of the two ReO_4^- tetrahedra by integration into the lattice of the low temperature modification.

i) Signal component A has no visible quadrupole coupling. The experimental line width can be approximated to 7 kHz. A maximum quadrupole interaction hidden under dipolar broadening can be calculated as $e^2qQ/h \approx 3$ MHz. ^{127}I NMR measurements on tetraphenylstibonium-metaperiodate show that quadrupole coupling constants in the range of 2 MHz $\leq e^2qQ/h \leq 30$ MHz can be determined with our Bruker CXP 200 NMR spectrometer [11]. It appears therefore that this group of ReO_4^- anions are not or very weakly distorted in the present lattice such that the electric field gradient almost disappears.

ii) Signal component B shows the two characteristic frequency edges of a second order quadrupole

splitting with a nearly axial-symmetric asymmetric parameter $\eta \approx 0$ [13, 14]. The frequency edges are broadened by dipole–dipole interactions. From Fig. 6 we can calculate a temperature coefficient $\bar{\alpha} \approx -1.5 \cdot 10^{-2}$ K^{-1} in the temperature range of 290 K $\leq$ T ≤ 330 K. This extremely negative value is in contradiction with the Bayer theory [15]. Obviously the occurrence of volume effects as defined by the Kushida-Benedek-Bloembergen (KBB) theory [16] cannot be neglected. Therefore the pressure coefficient $(\delta v/\delta p)_T$ corresponding to the KBB theory must possess a large positive value in order to yield an extremely negative value $(\delta v/\delta T)_p$.

From the temperature dependent quadrupole interactions we can gather a continuous change in the electric field gradient, which is caused by the distortion of the ReO$_4^-$ anion. With the aid of a point charge model for the ReO$_4^-$ ions it is possible to determine the deviation $\Delta\beta$ of the O–Re–O angle from the tetrahedron angle $\beta = 109.47°$ [17, 18]. The dependence of the quadrupole coupling constant upon $\Delta\beta$ is given by eq. (2):

$$e^2qQ/h = Z\,e^2Q/h\,r^3(9\cos^2\beta - 1)\,(1 - \gamma_\infty) \qquad (2)$$

with Z : electric charge of the oxygen atom,
β : O–Re–O angle,
γ_∞: Sternheimer polarization coefficient,
r : Re–O distance [19].

The results, depending on bond ionization, are listed in Table III.

Depending on the electric charge of the oxygen atoms, the $\Delta\beta$ values lie in the range of $0.14-0.56°$ at T $= 380$ K. These results demonstrate clearly the advantages of $[185]$Re and $[187]$Re solid state NMR spectroscopy. Quadrupole interactions are extremely sensitive to structural effects so that very small changes in the symmetry properties can easily be calculated. Even with X-ray measurements it is very

Table III. Deviation $\Delta\beta$ of the ReO$_4^-$ ions of (CH$_3$)$_4$AsReO$_4$ from tetrahedral symmetry.

T [K]	$\Delta\beta$ (°) ionic ($Z = -2$)	50% ionic ($Z = -1.25$)	covalent ($Z = -0.5$)
380	0.14	0.22	0.56
370	0.14	0.23	0.57
360	0.15	0.24	0.60
350	0.16	0.26	0.66
340	0.18	0.29	0.74
330	0.21	0.34	0.86
320	0.24	0.39	0.98
310	0.28	0.45	1.15

difficult to determine deviations $\Delta\beta$ in the range of $\Delta\beta < 0.5°$.

In the temperature range 294 K $\leq$ T ≤ 301 K we observe a reversible first order phase transition. It can be assumed that the quadrupole coupling constant of the low temperature modification is very large, which makes it accessible only by NQR methods, because it is impossible to achieve $[185]$Re or $[187]$Re NMR spectra in this temperature range. This kind of experiments is in progress, especially in order to examine if the phase transition is accompanied by a change in the temperature behaviour of the quadrupole coupling constant. Since this effect can be observed very often, we expect to have found another compound with an anomalous positive temperature coefficient $\bar{\alpha}$ [1, 9, 10], measureable only by pure NQR methods.

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