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Exploring the limits of ^{73}Ge solid-state NMR spectroscopy at ultrahigh magnetic field†

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The ultrahigh field natural abundance ^{73}Ge solid-state wide-line NMR study of germanium dichloride complexed with 1,4-dioxane and tetraphenylgermane yields the largest ^{73}Ge quadrupolar coupling constant determined by NMR spectroscopy to date and the first direct observation of ^{73}Ge chemical shift anisotropy.

As a third row element, Ge has similarities with both the lighter Group 14 elements, carbon and silicon, and the heavier Group 14 elements, tin and lead. Tetravalent germanium, like carbon and silicon, is the most common valence state encountered in germanium chemistry. Germynes, divalent germanium containing compounds, are also important both as reactive intermediates and as synthetically useful precursors.¹ Research into the chemistry of germanium is driven not only by the pursuit of novel molecular systems, but also by the use of germanium in important semiconductor materials such as transistors, fiber optic systems, and infrared optics.

In theory, germanium solid-state NMR (SSNMR) spectroscopy can be used as an approach for the direct characterization of Ge-containing materials as it could provide some key information on the bonding and local coordination environment around Ge. Even though the natural abundance of ^{73}Ge (7.73%), the only NMR-active isotope of germanium, is comparable to that of ^{29}Si (4.70%), ^{73}Ge NMR spectroscopy is extremely difficult because of its very low gyromagnetic ratio ($\gamma = -0.936 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$), resulting in its very low resonance frequency ($\nu_L = 13.9 \text{ MHz}$ at 9.4 T and $\nu_L = 31.4 \text{ MHz}$ at 21.1 T). ^{73}Ge is a quadrupolar nucleus with spin, $I = 9/2$, and has a large quadrupole moment ($Q = -0.196 \times 10^{-28} \text{ m}^2$).² Thus, in a non-symmetric environment, the presence of even a small electric field gradient (EFG) will inevitably produce a sizable quadrupolar interaction that severely broadens the central transition (CT), and therefore, reduces the sensitivity. The first solid-state ^{73}Ge NMR spectrum was reported in 1999 for Ge single crystals.³ Since then, there have been very few solid-state ^{73}Ge NMR spectra reported in the literature.^{4–10} In most cases, Ge is in a highly symmetric environment.

In the last decade, the increasing availability of ultrahigh field magnets together with the development of sensitivity enhancement techniques, such as quadrupolar Carr–Purcell–Meiboom–Gill (QCPMG)¹¹ and related sequences,^{12–14} have made the observation of low- γ quadrupolar nuclei more feasible in solids. Indeed, recent work showed that the ^{73}Ge QCPMG spectra of several polymorphs of GeO_2 can be observed at 21.1 T.¹⁵

Performing ^{73}Ge NMR experiments at very high field reduces the effect of second-order quadrupolar broadening and increases the Boltzman population difference of the CT, leading to an improved sensitivity. Working at the highest possible field also allows the chemical shift anisotropy (CSA) to be measured more accurately since the CSA is proportional to the magnetic field strength.

We are undertaking a systematic ^{73}Ge NMR study of germanium compounds at ultrahigh magnetic field. In this communication, we report the results of the ultrahigh field study of two representative germanium containing species: $\text{GeCl}_2 \cdot \text{dioxane}$ (a stabilized germylene) and GePh_4 (a prototypical organogermane). This work reveals two extreme situations: (1)

the extremely broad spectrum of the Ge(II) complex, which is entirely dominated by the quadrupolar interaction, leading to the largest ^{73}Ge quadrupolar coupling constant ($C_Q = 44\text{ MHz}$) ever determined by NMR spectroscopy and (2) for the first time, a ^{73}Ge CSA of 30 ppm was directly extracted from a very narrow spectrum of a Ge(IV) compound. First-principles theoretical calculations based on plane wave-pseudo potential density functional theory (DFT) have also been performed using the CASTEP^{16,17} program to predict the ^{73}Ge NMR parameters.

The 1,4-dioxane complex of germanium dichloride is used as a source of molecular GeCl_2 in the synthesis of numerous germanium compounds.¹ The complex crystallizes in space group $C2/c$.¹⁸ The structure consists of infinite chains of alternating GeCl_2 and $\text{C}_4\text{H}_8\text{O}_2$ molecules and contains one unique crystallographic Ge site (Fig. 1). The true coordination number of the Ge(II) is four [with two covalent bonds to two Cl (Ge-Cl distance = $2.2813(5)\text{ \AA}$) and two weak bonds to two O (Ge-O distance = $2.399(1)\text{ \AA}$ (typical Ge-O bond length: $1.75\text{--}1.85\text{ \AA}$)¹⁹) from two dioxane molecules]. However, there are two other non-bonded Cl atoms around Ge at a distance of $3.463(1)\text{ \AA}$, forming a pseudo-octahedral environment (Fig. 1(b)). The O-Ge-O bond angle is $173.15(6)^\circ$, while the Cl-Ge-Cl bond angle is $94.30(2)^\circ$. Our initial attempt to acquire a ^{73}Ge signal at 9.4 T failed completely. The acquisition of the ^{73}Ge signal of $\text{GeCl}_2\cdot\text{dioxane}$ was very difficult even at 21.1 T due to the low sensitivity and the broadness of the powder pattern. Since the CT spectrum was approximately 650 kHz wide, a total of 23 piecewise frequency-stepped QCPMG sub-spectra (Fig. S1, ESI†) had to be obtained (the acquisition time for each sub-spectrum was approximately 5 h). The co-added spectrum is shown in Fig. 2.

Fig. 1 Crystal structure of $\text{GeCl}_2\cdot\text{dioxane}$. (a) The chain structure of $\text{GeCl}_2\cdot\text{dioxane}$. (b) Ge pseudo-octahedral environment. (c) View along c -axis.

Fig. 2 ^{73}Ge static QCPMG NMR spectra of $\text{GeCl}_2\cdot\text{dioxane}$ at

The observed spectrum can be reasonably simulated without inclusion of the CSA, suggesting that the ^{73}Ge spectrum is dominated by the quadrupolar interaction. The C_Q of 44(2) MHz represents the largest value determined by ^{73}Ge NMR to date. The very large C_Q value originates from the nonspherical electronic environment around the Ge atom. The asymmetry parameter of the EFG tensor is 0.5(1). The non-axial symmetric EFG tensor is consistent with the fact that the site symmetry of Ge is only C_2 . The isotropic chemical shift (δ_{iso}) value is 1100(250) ppm. Despite the relatively large uncertainty, the δ_{iso} does indicate that the $^{73}\text{Ge(II)}$ nucleus in this compound is more deshielded than the Ge(II) in GeI_2 (−213 ppm)⁸ and the Ge(IV) nuclei in organogermanes reported in the literature.^{8–10} The CASTEP calculations predicted the following EFG parameters: $C_Q = 69.0$ MHz, $\eta_Q = 0.87$. Although the magnitude of the calculated parameters varies significantly from the observed values, the calculations correctly predict a very large C_Q value and a non-asymmetric EFG tensor. Several factors may cause the discrepancy between the observed and the calculated EFG tensor parameters using the CASTEP program.^{20,21} Inaccuracies in the crystal structure data may significantly affect the calculated parameters. However, even when the geometry of the germylene complex was optimized computationally, the agreement with the experimental parameters did not improve (Table S1). Dynamic motion in the lattice might account for the discrepancy. Indeed, the ^{13}C MAS NMR spectrum of the complex (not shown) consists of only a single peak, instead of two non-equivalent carbons as indicated by the crystal structure, suggesting that possible motions, such as ring wobbling, may partially contribute to a smaller observed C_Q .

Tetraphenylgermane (GePh_4) is a representative tetravalent organogermane. GePh_4 crystallizes in space group $P\bar{4}2_1c$.²² The Ge atom is tetrahedrally bonded to four C atoms. The high molecular symmetry and the Ge site symmetry (S_4) result in a single sharp peak under MAS conditions (Fig. 3(a)). The isotropic chemical shift (δ_{iso}) of −30 ppm is in excellent agreement with the chemical shift recorded in the MAS spectrum of GePh_4 previously reported by Takeuchi *et al.*⁴ In general, the chemical shielding (CS) tensor contains valuable information on bonding and structure. However, for quadrupolar nuclei, the CS tensor parameters often cannot be accurately extracted from the spectrum acquired at low- and moderate-field strength and, in many cases, the small CSA cannot be directly measured at all because when the large quadrupolar interaction dominates, the small CSA cannot manifest itself in the spectrum. As mentioned earlier and shown in several reports,^{21,23,24} this problem can be significantly alleviated by working at very high field due to the fact that the second-order quadrupolar interaction scales inversely and the CS interaction is proportional to the field strength.

Fig. 3 ^{73}Ge MAS (a) and static echo (b) NMR spectra of GePh_4 at 21.1 T. The simulated spectrum is shown in (c). (d) shows the direction of the unique CS tensor component.

[Fig. 3\(b\)](#) shows proton-decoupled ^{73}Ge static echo spectrum of GePh_4 observed at 21.1 T. The spectrum exhibits a typical axially-symmetric CSA powder pattern, indicating the CSA significantly affects the appearance of the spectrum. The spectral simulation ([Fig. 3\(c\)](#)) produces a span (Ω) of 30(3) ppm. The skew ($\kappa = -1$) indicates that the ^{73}Ge CS tensor is axially symmetric, which is consistent with the S_4 site symmetry at Ge. The high local symmetry yields a very small C_Q with an estimated upper limit of 0.3 MHz ($\eta_Q = 0$). Although C_Q is very small, it is not zero. The existence of a small quadrupolar interaction is clearly indicated by the spinning-side bands due to satellite transitions (STs) in the MAS spectrum ([Fig. S2a](#), [ESI†](#)). The full static spectrum together with the simulated one including STs ([Fig. S2b,c](#), [ESI†](#)) also shows the broad signals of STs. The combination of the very small quadrupolar interaction and working at ultrahigh field results in the first direct observation of ^{73}Ge CSA. The negative sign of skew indicates that the δ_{11} is the unique CS tensor component. To obtain the CS tensor direction, CASTEP calculations were performed ([Table S2](#), [ESI†](#)). The initial calculations using the published crystal structure metrics²² predicted the following spectral parameters: $\delta_{\text{iso}} = -8$ ppm, $\Omega = 30$ ppm, $\kappa = -1$, $C_Q = 1.65$ MHz, $\eta_Q = 0$. After structure optimization, the predicted parameters ($\delta_{\text{iso}} = -30$ ppm, $\Omega = 29$ ppm, $\kappa = -1$, $C_Q = 0.15$ MHz, $\eta_Q = 0$) are in better agreement with the experimentally determined parameters. The most shielded (unique) component of the CS tensor, δ_{11} , is oriented along the direction bisecting the C–Ge–C' angle (along the 2-fold axis at Ge and with a C–Ge– δ_{11} angle = 54.59°) ([Fig. 3d](#)).

In summary, this work demonstrates that natural abundance solid-state ^{73}Ge wide-line NMR spectra of germanium compounds where the Ge experiences an extremely large quadrupolar interaction can be obtained. Also, at ultrahigh magnetic field and under favourable circumstances, the very small ^{73}Ge CSA can be directly measured. These results reveal the possibility for the direct examination of ^{73}Ge spectra and the correlation of ^{73}Ge NMR parameters with bonding and local structure around Ge center in organogermanes and germynes with a wide range of substituents.

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Notes and references

- 1 Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511 [Article](#) [ChemPort](#) .
- 2 P. Pyykko, *Mol. Phys.*, 2008, **106**, 1965–1974 [Article](#) [ChemPort](#) .
- 3 S. V. Verkhovskii, A. Y. Yakubovskii, A. Trokiner, B. Z. Malkin, S. K. Saikin, V. I. Ozhogin, A. V. Tikhomirov, A. V. Ananyev, A. P. Gerashenko and Y. V. Piskunov, *Appl. Magn. Reson.*, 1999, **17**, 557–576 [Article](#) [ChemPort](#) .
- 4 Y. Takeuchi, M. Nishikawa, K. Tanaka, T. Takayama, M. Imanari, K. Deguchi, T. Fujito and Y. Sugisaka, *Chem. Commun.*, 2000, 687–688 [RSC Article](#) .
- 5 Y. Takeuchi, M. Nishikawa, K. Tanaka and T. Takayama, *Chem. Lett.*, 2001, 572–573 [Article](#) [ChemPort](#) .
- 6 J. F. Stebbins, L.-S. Du, S. Kroeker, P. Neuhoﬀ, D. Rice, J. Frye and H. J. Jakobsen, *Solid State Nucl. Magn. Reson.*, 2002, **21**, 105–115 [Article](#) [ChemPort](#) .
- 7 S. V. Verkhovskii, A. Y. Yakubovsky, B. Z. Malkin, S. K. Saikin, M. Cardona, A. Trokiner and V. I. Ozhogin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 104201 [Article](#) .
- 8 Y. Takeuchi, M. Nishikawa and H. Yamamoto, *Magn. Reson. Chem.*, 2004, **42**, 907–909 [Article](#) [ChemPort](#) .
- 9 Y. Takeuchi, M. Nishikawa, H. Hachiya and H. Yamamoto, *Magn. Reson. Chem.*, 2005, **43**, 662–664 [Article](#) [ChemPort](#) .
- 10 Y. Takeuchi and T. Takayama, *Annu. Rep. NMR Spectrosc.*, 2005, **5**, 155–200 [ChemPort](#) .
- 11 F. H. Larsen, H. J. Jakobsen, P. D. Ellis and N. C. Nielsen, *J. Phys. Chem. A*, 1997, **101**, 8597–8606 [Article](#) [ChemPort](#) .
- 12 R. W. Schurko, I. Hung and C. M. Widdifield, *Chem. Phys. Lett.*, 2003, **379**, 1–10 [Article](#) [ChemPort](#) .
- 13 R. Siegel, T. T. Nakashima and R. E. Wasylishen, *Chem. Phys. Lett.*, 2004, **388**, 441–445 [Article](#) [ChemPort](#) .
- 14 L. A. O'Dell and R. W. Schurko, *Chem. Phys. Lett.*, 2008, **464**, 97–102 [Article](#) [ChemPort](#) .
- 15 V. K. Michaelis, P. M. Aguiar, V. V. Terskikh and S. Kroeker, *Chem. Commun.*, 2009, 4660–4662 [RSC Article](#) .
- 16 M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens.*

Matter, 2002, **14**, 2717–2744 [Article](#) [ChemPort](#) .

- 17 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567–570 [Article](#) [ChemPort](#) .
- 18 M. K. Denk, M. Khan, A. J. Lough and K. Shuchi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 1830–1832 [Article](#) .
- 19 K. M. Baines and W. G. Stibbs, *Coord. Chem. Rev.*, 1995, **145**, 157–200 [Article](#) [ChemPort](#) .
- 20 C. M. Widdifield and D. L. Bryce, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7120–7122 [RSC Article](#) .
- 21 I. Moudrakovski, S. Lang, S. Patchkovskii and J. Ripmeester, *J. Phys. Chem. A*, 2010, **114**, 309–316 [Article](#) [ChemPort](#) .
- 22 P. C. Chieh, *J. Chem. Soc. A*, 1971, 3243–3245 [RSC Article](#) .
- 23 D. L. Bryce, E. B. Bultz and D. Aebi, *J. Am. Chem. Soc.*, 2008, **130**, 9282–9292 [Article](#) [ChemPort](#) .
- 24 M. A. M. Forgeron and R. E. Wasylshen, *Phys. Chem. Chem. Phys.*, 2008, **10**, 574–581 [RSC Article](#) .
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Footnote

† Electronic supplementary information (ESI) available: Experimental details, ^{73}Ge static piecewise-frequency stepped QCPMG NMR spectra of $\text{GeCl}_2\cdot\text{dioxane}$, ^{73}Ge MAS and static echo NMR spectra of GePh_4 , calculated ^{73}Ge NMR parameters using CASTEP. See DOI: [10.1039/b926071d](https://doi.org/10.1039/b926071d)