

⁷³Ge solid-state NMR investigation of germanium halides using ultrahigh magnetic fields and DFT calculations

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Germanium is a key component in many types of materials, conferring useful properties on semiconductors, optical and mesoporous materials. Nuclear magnetic resonance (NMR) appears to be an attractive technique characterisation of such materials, although the intrinsic properties of the ⁷³Ge nucleus (including a low magnetogyric ratio and low natural abundance) present experimental difficulties. Ultrahigh magnetic fields raise the resonance frequency of ⁷³Ge (31.4 MHz at 21.1 T), resulting in a more favourable population difference and correspondingly increased sensitivity, while simultaneously mitigating probe-ringing effects.

Two series of germanium halides, GeX₂ and GeX₄ (where X = Cl, Br, and I), were investigated to study the electric field gradient (EFG) characteristics of ⁷³Ge and to observe any differences that may occur between oxidation states. The higher symmetry species show that ⁷³Ge possesses small C_Q values, but very slight distortions from cubic symmetry result in marked C_Q increases (Figure 1). Comparing the two oxidation states of germanium, there is significantly less variation in the germanium (IV) halides than germanium (II) halides with regard to the C_Q magnitude. All C_Q values for the GeX₄ compounds are within 1-2 MHz, whereas the GeX₂ compounds show a greater range of 0-35 MHz.

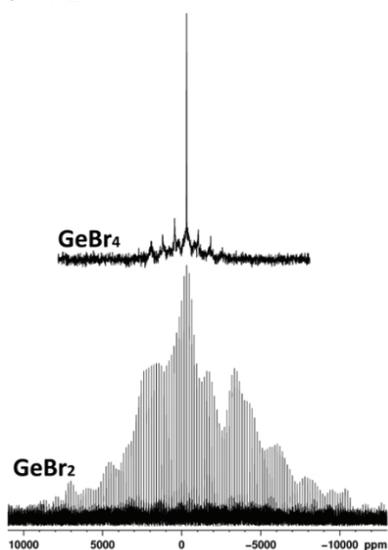


Figure 1: ⁷³Ge NMR of GeBr₄ and GeBr₂ at 21.1 T, showing the extreme difference in EFG environments.

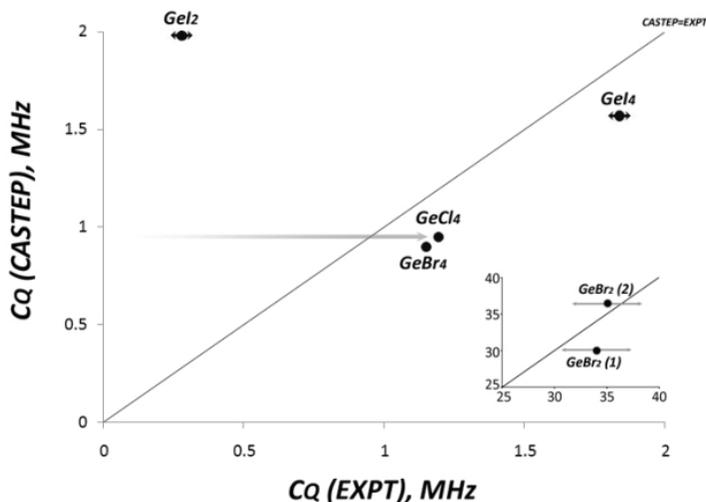


Figure 2: Comparison of CASTEP and experimental C_Qs; most are underestimated, while GeI₂ is a suspicious outlier.

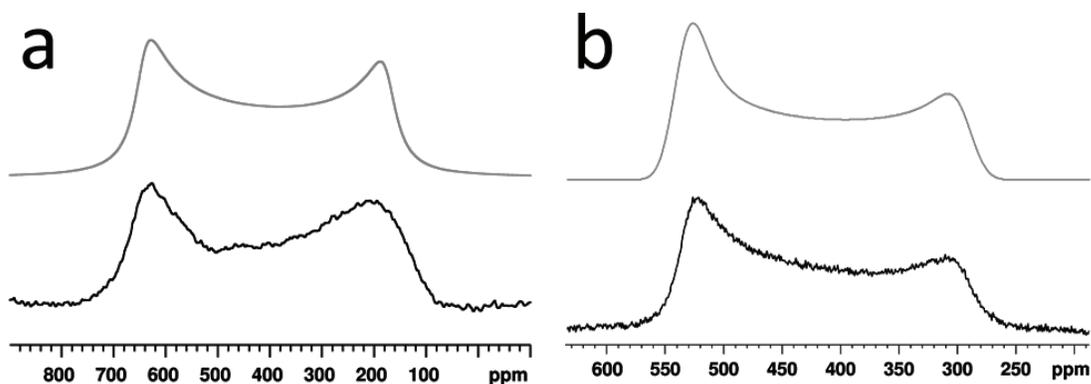


Figure 3: ^{127}I NMR of GeI_2 at (a) 14.1 T and (b) 21.1 T, with simulations (above), reflecting the highly symmetric iodine environment through the observed low C_Q .

A DFT study using CASTEP software complements the experimental data and provides a link to the molecular geometries. The calculations reveal a fairly accurate prediction of C_Q values, with a slight underestimate observed in most cases (Figure 2). We have obtained parallel results from CASTEP calculations of germanium oxides [1,2]. Interestingly, the calculations reveal a significant discrepancy for GeI_2 . Our NMR experiments indicate that the GeI_2 C_Q is less than 0.3 MHz, while the calculated value is almost an order of magnitude *larger*. Although there have been a number of crystal structures reported in the literature, we have used the most recent for our calculation, which is highly symmetrical [3]. Using ^{127}I NMR experiments as an alternative view, we find a relatively small quadrupolar coupling for the iodine site (~ 8 MHz, Figure 3), while CASTEP predicts $C_Q = 16$ MHz. Adjusting the geometry of the CASTEP input to match the experimental data yields a chemically unrealistic structure, suggesting that CASTEP struggles to calculate small deviations from cubic symmetry.

The ^{73}Ge and ^{35}Cl quadrupolar interactions determined for GeCl_2 facilitate predictions about this unknown structure. Previous proposals that GeCl_2 is isostructural with GeBr_2 are clearly incorrect, considering the very large C_Q s in the latter (Figure 1). Much more likely is that GeCl_2 is isostructural with GeI_2 . These systems provide ideal conditions for "NMR crystallography".

References

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- [3] E. Urgiles, P. Melo, C.C. Coleman, *J. Cryst. Growth* **165** (1993) 245-249.