The quadrupole coupling constant $C_Q$ and the asymmetry parameter $\eta$ have been determined for two complex aluminium hydrides from $^{27}$Al NMR spectra recorded for stationary samples by using the Solomon echo sequence. The thus obtained data for KAlH$_4$ ($C_Q=(1.30 \pm 0.02)$ MHz, $\eta=(0.64 \pm 0.02)$) and NaAlH$_4$ ($C_Q=(3.11 \pm 0.02)$ MHz, $\eta<0.01$) agree very well with data previously determined from MAS NMR spectra. The accuracy with which these parameters can be determined from static spectra turned out to be at least as good as via the MAS approach. The experimentally determined parameters ($\delta_{\text{exp}}$, $C_Q$ and $\eta$) are compared with those obtained from DFT-GIPAW (density functional theory – gauge-including projected augmented wave) calculations. Except for the quadrupole coupling constant for KAlH$_4$, which is overestimated in the GIPAW calculations by about 30%, the agreement is excellent. Advantages of the application of the Solomon echo sequence for the measurement of less stable materials or for in situ studies are discussed.

Introduction

Complex aluminium hydrides have been studied rather extensively in the past two decades, mainly because of their potential application as hydrogen storage materials. Triggered by the seminal paper by Bogdanović and Schwickardi,[1] the reversible dehydrogenation of NaAlH$_4$ under the influence of catalysts was the target of many experimental and theoretical studies. In the course of these investigations, a large number of materials containing aluminium hydrides have been proposed for the reversible storage of hydrogen. Several new complex aluminium hydrides have been discovered and characterized. The progress in this research area has regularly been reviewed from different perspectives.[2–10]

Beside diffraction methods, NMR spectroscopy has been proven to be a valuable tool for the identification and quantification of the various aluminium hydrides that might be present in the samples under study.[11–25] Most of the $^{27}$Al NMR spectra reported for aluminium hydrides were recorded under MAS conditions, i.e. for samples spinning fast around an axis that is inclined by an angle of 54° 44' 27" relative to the direction of the magnetic field. This technique is one of the standard methods to tackle the resolution problems in solid-state NMR spectroscopy. It significantly reduces the line broadening caused by second-order quadrupole interaction and removes the broadening brought about by the heteronuclear dipole-dipole interaction as well as by the anisotropy of the chemical shift.[26] The thus improved spectral resolution allows the aluminium hydride species to be identified by the position of the centreband of the central transition. $^{27}$Al NMR spectra measured by using more sophisticated methods that were developed in the quest for further enhanced spectral resolution, such as multi-quantum (MQ) MAS,[27,28] have rarely been reported for aluminium hydrides so far.[11,15,16,20] It should be noted that there are cases where the approach of using fast sample spinning is bound to fail. If the quadrupole interaction is as strong as for instance recently found for the aluminium nuclei in Mg(AlH$_4$)$_2$[29] or in an alane amine adduct,[30] the static linewidth of the central transition at the usually available magnetic fields exceeds the available spinning speeds by far. Nevertheless, $^{27}$Al NMR spectra can be recorded for non-spinning samples by an echo technique and can be used to characterize these materials.

Quadrupole interaction should not so much be regarded as an obstacle for recording highly resolved NMR spectra of solids, but first and foremost as a valuable source of information difficult to be gathered by other means. Any nucleus with a spin $I > 1/2$ has a non-vanishing electric quadrupole moment that interacts with the electric field gradient (EFG) at the site of the nucleus. This interaction influences the NMR frequency of the nucleus studied. Hence, any quadrupole nucleus can be regarded as a probe of the local geometry in general and of the symmetry in particular. Apart from the orientation of its principal axes system, the quadrupole coupling can be fully described by just two parameters: the so-called quadrupole
coupling constant $C_Q$, which is proportional to both the strength of the field gradient and the electric quadrupole moment of the nucleus under study, and the asymmetry parameter $\eta$ of the EFG.\cite{32,33,34} For example, if the nucleus is located on a symmetry axis $C_n$ with $n \geq 3$, the EFG is axially symmetric and $\eta$ is zero. In a cubic environment, there is no gradient and hence there is no quadrupole interaction.

For materials where the quadrupole interaction is small (or medium sized), the second-order quadrupolar broadening of the central transition is hardly noticeable or causes only a small splitting of a few ppm in the $^{27}$Al MAS NMR spectra. However, these spectra contain much more information than only the isotropic chemical shift. The range over which the spinning sidebands of the satellite transitions spread and the characteristic intensity modulations of these sidebands allow the parameters of the quadrupole interaction to be determined very precisely. This has been shown for NaAlH$_4$\cite{35} and KAlH$_4$.\cite{36}

The major aim of the present paper is to demonstrate that the information about the chemical shift and the quadrupole origin is well understood,\cite{34,35} Solomon echoes have rarely been used to observe the satellite transitions in solid-state $^{27}$Al NMR spectroscopy.\cite{37} The precision of NMR data obtained from stationary samples is generally assumed to be lower than that of those derived from MAS NMR spectra. However, a systematic study has shown that in many cases static spectra provide more reliable data for tensor parameters than those obtained for spinning samples, with the exception of the measurement of the anisotropy of the chemical shift, for which an optimum number of spinning sidebands was found.\cite{38} Avoiding fast sample spinning is certainly advisable for less stable materials that are prone to decomposition under mechanical and/or thermal stress.

With the above discussed high sensitivity of the quadrupole interaction to the local environment of the nucleus, the precise determination of the quadrupole coupling parameters combined with DFT (density functional theory) calculations can offer an alternative approach to high-quality structures for polycrystalline materials.\cite{38} We show that the experimental data obtained for NaAlH$_4$ and KAlH$_4$ are well reproduced by DFT-GiPaw (gauge-including projected augmented wave) calculations.\cite{38}

Results and Discussion

Experimental Results for KAlH$_4$

Figure 1 shows a $^{27}$Al NMR spectrum obtained as a Fourier transform of the Solomon echo (formed at $\tau$ after the second pulse) for a stationary KAlH$_4$ sample in comparison with the best fit. The depicted lineshape is typical of a first-order quadrupolar broadened powder spectrum.\cite{39} The positions of the characteristic discontinuities of the lineshape are obviously nicely reproduced by the fit. The significantly reduced intensity in the outer wings of the experimental spectrum is mainly caused by the insufficient excitation width of the finite pulses used.\cite{40} Neither the finite excitation width nor the finite bandwidth of the NMR probe are taken into account by the simulation program used. It should be noted that the resonance line of the central transition is not caused by the Solomon echo but by the free induction decay following the second pulse of the pulse sequence.\cite{35}

The complex resonance line can be described by only three parameters: the position of the line is mainly determined by the isotropic chemical shift $\delta_{iso}$ and its shape is governed by the quadrupole coupling constant $C_Q$ and the asymmetry parameter $\eta$.\cite{34} The latter two parameters also have a small but significant effect on the line position via the quadrupole induced shift $\delta_{qis}$. This second-order effect that is inversely proportional to the square of the magnetic field applied influences the centre of gravity of the central transition and each pair of satellite transitions in a characteristic way. Hence, the line position read off a spectrum must generally be corrected to obtain the true chemical shift for any half-integer quadrupolar nucleus. Simulation programs take the quadrupole induced shift into account.

It should be noted that from the NMR measurements reported here, only the magnitude, but not the sign of the quadrupole coupling constant $C_Q$ can be determined. The resonance lines of every pair of satellite transitions are mirror images of each other. In accordance with most of the NMR literature,\cite{31} we omit the absolute value bars for $C_Q$ throughout the paper.

To have a suitable simulation program at hand is useful, but not essential for determining the spectral parameters from experimental spectra measured for stationary samples. In fact,
rather good estimates of these parameters can directly be read off the experimental spectrum in Figure 1. The maxima of the inner satellite transitions at 380 and −162 ppm yield a value of 109 ppm for the centre of gravity of these transitions. Since for any nucleus with \( I = 5/2 \), the position of the centre of gravity of the inner satellite transitions is known to be much closer to the isotropic chemical shift than the centre of gravity of the central transition,\(^{[41]} \) this estimate is very close to the true isotropic chemical shift \( \delta_{\text{iso}} = (108 \pm 2) \) ppm found by means of the simulation program.

The quadrupole coupling constant \( C_Q \) can be derived from the total spread of the satellite transitions \( \Delta \nu_s(3/2) \). For the inner satellite transitions \((m = 3/2)\), the following relation holds:\(^{[25,40,42]} \)

\[
C_Q = \frac{10}{3} \Delta \nu_s(3/2). \tag{1}
\]

Since the outermost shoulders of the inner satellite transitions are localized at 1610 ppm (low-field) and −1390 ppm (high-field), we have a total spread of 3000 ppm corresponding to \( \Delta \nu_s(3/2) \approx 390 \) kHz. With Eq. (1), this value leads to the rather good estimate of \( C_Q \approx 1.3 \) MHz. The asymmetry parameter can be estimated from the ratio of the splitting of the maxima \( \Delta \nu_s(m) \) to the total spread of any pair of satellite transitions according to the following equation:\(^{[25]} \)

\[
\eta = 1 - \frac{2 \Delta \nu_s(m)}{\Delta \nu_s}. \tag{2}
\]

With the above given values for the positions of the maxima of the inner satellite transitions, we find a splitting of 542 ppm corresponding to \( \Delta \nu_s(3/2) \approx 71 \) kHz. With Eq. (2), we obtain \( \eta \approx 0.64 \). Of course, the quadrupole parameters can also be obtained from the outer satellite transitions, but the discontinuities are usually much better defined for the narrower inner satellite transitions. The estimates for \( C_Q \) and \( \eta \) turned out to be so precise that they could not be improved by means of the simulation program. We think that the margins of error given for \( C_Q \) \( (\pm 20 \text{ kHz}) \) and \( \eta \) \( (\pm 0.02) \) in Table 1 are rather conservative estimates. Hence, the reliability of determining the parameters of the quadrupole coupling for KAlH\(_4\) from static spectra is as good as that from spectra measured under MAS conditions.\(^{[25]} \) Regarding the precision of the determination of the isotropic chemical shift, the MAS approach is definitely superior.

Figure 2 compares the \(^{27}\text{Al} \) NMR spectra measured with and without MAS with the simulated spectra using the parameters previously determined from MAS spectra measured at different spinning speeds. The quality of the fits can better be judged from the enlarged version of Figure 2 given as Figure S2 in the Supporting Information. Even the tiny amount of the cryolite-like by-product NaAlH\(_4\) detected as narrow line at \( -427 \text{ ppm} \) in the MAS NMR spectrum\(^{[25]} \) can also be identified as shoulder at about \(-40 \text{ ppm} \) in the static spectrum.

Although the lineshape simulations neglect the effect of a possible anisotropy of the chemical shift, they reproduce the experimental lineshapes quite well. Hence, any anisotropy must be rather small and contributes only to the line broadening of the static spectrum. This observation is in line with the results of our GIPAW calculations. For the span \( \Omega \), a parameter describing the total spread of a resonance line governed by chemical shift anisotropy,\(^{[41]} \) these calculations yield a value of 11 ppm corresponding to less than 1.5 kHz (see Supporting Information, Table S1).

| Material | Method | \( \delta_{\text{iso}}/\text{ppm} \) | \( C_Q/\text{MHz} \) | \( \eta \) |
|----------|--------|-----------------|-----------------|--------|
| KAlH\(_4\) | SPE, MAS\(^{[25]} \) | 107.6 ± 0.2 | 1.29 ± 0.02 | 0.64 ± 0.02 |
| SE, static | 108 ± 2 | 1.30 ± 0.02 | 0.64 ± 0.02 |
| GIPAW | 108.4/107.8 | 1.69 | 0.59 |
| NaAlH\(_4\) | SPE, MAS\(^{[25]} \) | 97.5 | 3.15 | 0.04 |
| SPE, MAS | 97.2 ± 0.3 | 3.11 ± 0.03 | < 0.05 |
| SPE, static\(^{[2]} \) | 101 ± 3 | 3.08 | 0 |
| SPE, static\(^{[2]} \) | 99 ± 3 | 3.11 ± 0.02 | < 0.01 |
| SE, static | 99 ± 3 | 3.11 ± 0.02 | < 0.01 |
| GIPAW | 95.4/96.1 | 3.14 | 0 |

Figure 2. Experimental \(^{27}\text{Al} \) NMR spectra of KAlH\(_4\) measured for a stationary sample (blue) and the same sample spinning at \( \nu_{\text{MAS}} = 1.4 \text{ kHz} \) (black) and their simulations (green and red, respectively) with the parameters \( \delta_{\text{iso}} = 107.6 \text{ ppm} \), \( C_Q = 1.29 \text{ MHz} \) and \( \eta = 0.64 \). To ease the comparison, the simulated spectra have been inverted.
Experimental Results for NaAlH₄

Figure 3 shows a $^{27}$Al NMR spectrum of NaAlH₄ obtained as a Fourier transform of the Solomon echo for a stationary sample in comparison with the best fit. Again, the lineshape is typical of a first-order quadrupolar broadened powder spectrum, but this time for the case of an axially symmetric EFG tensor, i.e. $\eta = 0$. Apart from the central transition, the spectrum shows the sharp maxima of the four satellite transitions. These maxima correspond to the perpendicular components of the axially symmetric EFG tensor. The maxima of the inner satellite transitions are found at about 1887 and $-1674$ ppm, corresponding to a splitting of the maxima $\Delta v_{Q}(3/2)$ of about 464 kHz. Since, for $\eta = 0$, the total spread $\Delta v_{Q}(m)$ equals $2\Delta v_{Q}(m)$ (see Eq. (2)), we obtain with Eq. (1) a value of $C_Q \approx 3.09$ MHz as an estimate of the strength of the quadrupole coupling. Using the simulation program, we found for the best fit $C_Q = 3.11$ MHz.

As expected from the known structure of NaAlH₄, we found no indication for a deviation from axial symmetry. Since the Al atoms are located in Wyckoff position 4b, i.e. on a $\Delta z$ axis, the asymmetry parameter $\eta$ is bound to be zero. However, with the finite linewidth observed, it is difficult to verify experimentally that $\eta = 0$ holds. From our experimental data, we can safely deduce that $\eta < 0.01$ is the upper bound for a deviation from axial symmetry.

Because of the enormous width of the spectrum, the deviations of the experimental from the simulated lineshape are more pronounced than in the case of KAlH₄. From the above given splitting of the maxima of the inner transition $\Delta v_{Q}(3/2)$, it follows that the total spread of the outer satellite transition $\Delta v_{Q}(5/2)$ is about 1.86 MHz. In particular, the shoulders of the outer satellite transition can not be discerned in the experimental spectrum. However, these distortions of the lineshape are less severe than for spectra obtained from the free induction decay after a single pulse. During the inevitable receiver dead time after the pulse, the fast decaying signal corresponding to the broad features is lost and only the sharp maxima can be seen in these spectra. It seems unlikely that this approach could produce meaningful results for the quadrupole parameters for the general case $\eta \neq 0$. In our own attempts to record $^{27}$Al NMR spectra for stationary NaAlH₄ samples by single pulse excitation, we ran into serious phasing problems.

Figure 4 compares the $^{27}$Al NMR spectra measured with and without MAS with the simulated spectra using the parameters determined from MAS spectra measured at different spinning speeds. The quality of the fits can better be judged from the enlarged version of Figure 4 given as Figure S3 in the Supporting Information. As for KAlH₄ we do not see any of the characteristic effects of a possible anisotropy of the chemical shift in the spectra recorded for stationary samples or under MAS conditions. Our GIPAW calculations yield a value of about 19 ppm for the span $\Omega$, corresponding to about 2.5 kHz.

As distinct from the case of KAlH₄ at the same field strength, the effect of second-order quadrupole interaction is not fully masked by other broadening mechanisms. The centreband of the central transition shown in Figure 5 exhibits two maxima separated by about 3 ppm (95.6 and 92.3 ppm). These maxima are best resolved at spinning rates between 3 and 6 kHz. We assume that the reduced resolution at higher spinning rates is caused by frictional heating that leads to a

![Figure 3](image1.png)

**Figure 3.** Experimental $^{27}$Al NMR spectrum of NaAlH₄ obtained from a Solomon echo generated with a pulse spacing of 600 µs (blue) and the best fit of this spectrum (green) using the following parameters: $\delta_{iso} = 99$ ppm, $C_Q = 3.11$ MHz and $\eta = 0$. Lorentzian line broadening with $LB = 3000$ Hz and $LB = 4000$ Hz was applied for the experimental spectrum and the simulated spectrum, respectively. The experimental spectrum is cut off at about 12% of the maximum intensity of the central line.

![Figure 4](image2.png)

**Figure 4.** Experimental $^{27}$Al NMR spectra of NaAlH₄ measured for a stationary sample (blue) and the same sample spinning at $\nu_{MAS} = 10$ kHz (black) and their simulations (green and red, respectively) with the parameters $\delta_{iso} = 97.2$ ppm, $C_Q = 3.11$ MHz and $\eta = 0$. To ease the comparison, the simulated spectra have been inverted.
significant increase of the temperature in certain parts of the sample that influences the chemical shift and/or the quadrupole coupling parameters. Insufficient decoupling is likely to contribute to the non-perfect lineshape observed. We have used the SPINAL-64 sequence without any further optimization that has been shown to be crucial for optimum performance of proton decoupling sequences.

However, Figure 5 shows that the splitting and the general lineshape of the centreband can nicely be fitted using the same parameters as for the simulated spectra of the satellite transitions in Figure 4. At the still rather low ratio of the quadrupole coupling constant to the resonance frequency \( C_\text{Q}/v_0 \approx 0.024 \), the experimental lineshape of the centreband of the central transition does not really show the discontinuities characteristic for second-order quadrupolar broadening. Hence, the determination of the parameters of the quadrupole coupling from the experimental spectrum in Figure 5 is certainly not the most reliable method. These parameters can be obtained with much higher accuracy from the satellite transitions governed by first-order quadrupole interaction, either from spectra of stationary samples measured by means of the Solomon echo sequence or from the characteristic sideband patterns of MAS spectra measured with single-pulse excitation. Since the second-order broadening is proportional to the inverse of the square of the quadrupole coupling constant, the lineshape of the centreband of the central transition can, of course, not deliver any information about the sign of \( C_\text{Q} \) either.

GIPAW vs Experiment

The results from the DFT-GIPAW calculations are collected in Table 1, where experimental values from this study and previous work are given for comparison. With regard to the \(^{27}\text{Al}\) chemical shifts, both the use of \( \text{LiAlH}_4 \) as sole reference system (Eq. (3), see DFT-GIPAW Calculations in Experimental and Computational Methods) and the calculation by means of a linear regression over several alkali aluminium hydrides (Eq. (4)) deliver very good agreement with experiment. While the former approach should be suitable for converting DFT-computed chemical shieldings into chemical shifts for structurally closely related systems, the regression-based approach can be expected to be more broadly applicable for diverse alkali aluminium hydrides. The direct results of the DFT-GIPAW calculations \( (C_{\text{G}}, \eta, \eta_0) \) for all substances mentioned are summarised in Table S1 (Supporting Information).

The DFT-GIPAW quadrupole coupling constant \( C_{\text{Q}} \) of \( \text{KAlH}_4 \) is approximately 30% (0.4 MHz) larger than the experimental values. A similar overestimation was found in a previous DFT-GIPAW study of \( \text{Na}_4\text{AlH}_6 \). In that study, the observed difference was attributed to the influence of thermal motion on the electric field gradients, which is not taken into account in static DFT calculations. Although we cannot corroborate this hypothesis without further calculations, we may note the high sensitivity of the DFT-GIPAW quadrupole coupling constant to the structural parameters: Direct use of experimental structure data of \( \text{KAlH}_4 \) without optimization of the atomic coordinates, delivered a \( C_{\text{Q}} \) value of 6.5 MHz, thus deviating much more significantly from experiment than the result obtained for the optimized structure. In contrast, our calculated quadrupole coupling constant for \( \text{NaAlH}_4 \) is in perfect agreement with the experimental one. It is important to note that our procedure is different from that applied by Zhang et al. These authors used the experimentally determined value for \( C_{\text{Q}} \) and the calculated field gradient of \( \text{NaAlH}_4 \) to determine the quadrupole moment \( Q(\text{Al}) \). The thus obtained quadrupole moment was then used to calculate the quadrupole couplings for the other alanates investigated. Our calculations of the parameters of the quadrupole interaction are solely based on the crystallographic data and the generally accepted value of the quadrupole moment \( Q(\text{Al}) = 146.6 \text{mbarn} \). Hence, the calculated data reported here are fully independent from our experimental data.

Recently, a slightly higher value of the quadrupole moment \( Q(\text{Al}) = 148.2 \text{mbarn} \) was recommended on the basis of highly accurate coupled cluster calculations with single, double, and perturbative triple excitations (CCSD(T)) for Al-containing molecules. By using this value, the magnitudes of the calculated quadrupole coupling constants would be about 1% higher than given in Table 1 and Table S1 (Supporting Information). DFT calculations carried out with the newly recommended value for the quadrupole moment typically resulted in \( C_{\text{Q}} \) values deviating by about 10 to 15% from experiment.

With regard to the asymmetry parameters, the DFT-calculated \( \eta = 0.59 \) for \( \text{KAlH}_4 \) agrees very well with the experimental values, both from the literature and from the present work. For \( \text{NaAlH}_4 \), \( \eta = 0 \) reflects the high symmetry of the local environment (site symmetry: \( 4_l \)). All four \( \text{Al–H} \) bonds are equivalent by symmetry.
Although not in the focus of the present paper, we want to mention the GIPAW results for the counterions. We obtained a good agreement between experiment and calculations for the quadrupole parameters for $^{27}$K in KAlH$_{4}$: $Q_0 = 0.562/0.68$ MHz (Exp.[20]/GIPAW) and $\eta = 0.74/0.79$. Unfortunately, the result for $^{23}$Na in NaAlH$_{4}$ is less encouraging: $Q_0 = 0.15/0.46$ MHz (Exp.[19]/GIPAW) and $\eta = 0/0$. As mentioned above, we omit the sign of $Q_0$ for the experimental data.

**Conclusion**

For two complex aluminium hydrides, we have shown that by in situ operaendo studies of reactions at high pressure in a wide temperature range are easier to accomplish for stationary samples than for those under MAS conditions. Although there has been significant progress in developing appropriate MAS equipment,[31,52] in situ or operaendo NMR measurements are usually performed on static samples using hardware specially adapted to enable the reaction conditions to be reproduced as closely as possible.[53] Hence, the application of the Solomon echo sequence should be considered a valuable instrument in the NMR toolbox.

The use of Solomon echoes is certainly not limited to $^{27}$Al in aluminium hydrides, but should be feasible for other half-integer quadrupolar nuclei with small or moderate quadrupole couplings in materials from various classes of substances, provided that relaxation is slow enough for intense Solomon echoes to be formed.

The encouraging agreement between experimental and GIPAW data obtained is in line with the general notion that modern density functional theory is accurate enough to provide a good description of the electronic structure and, consequently, the EFG and quadrupole coupling in a very wide range of solids.[34] Hence, by determining the parameters of the quadrupole coupling, both from NMR measurements and DFT calculations, it should be possible to distinguish between different structural models for new materials based on diffraction data.

**Experimental and Computational Methods**

**Materials**

NaAlH$_{4}$ (Chemetall, 82–85%) was purified by dissolving it in tetrahydrofuran and filtering off the insoluble portions. The pure NaAlH$_{4}$ was precipitated from the solution by addition of pentane and carefully dried in vacuum.

KAIH$_{4}$ was produced by ball milling NaAlH$_{4}$ and KCl.[25] The resulting powder was suspended in diglyme. After filtration, KAIH$_{4}$ was precipitated through the addition of toluene and filtered off. The dried KAIH$_{4}$ contained small amounts of unreacted NaAlH$_{4}$ which were removed by treatment in tetrahydrofuran.

All syntheses and operations were performed under argon using dried and oxygen-free solvents. The zirconia MAS rotors (4 mm outer diameter) were filled and capped in a glove box and transferred to the spectrometer in argon-filled vials.

**Solid-state NMR Spectroscopy**

The $^{27}$Al NMR spectra were recorded on a Bruker Avance III HD 500WB spectrometer using double-bearing MAS probes (DVT BL4) at resonance frequencies of 130.3 MHz. The chemical shift was referenced relative to an external 1.0 M aqueous solution of aluminium nitrate. The same solution was used for determining the flip-angle. For the $^{27}$Al MAS NMR spectra, single $\pi/12$ pulses ($t_p = 0.6 \mu$s) were applied at a repetition time of 2 s (2,000–16,000 scans) and spinning frequencies ($\nu_{MAS}$) between 1.4 and 13 kHz. High-power proton decoupling (SPINAL-64)[34] was used for all $^{27}$Al NMR spectra shown in this paper. The magic angle was adjusted by maximizing the rotational echoes of the $^{27}$Na resonance of solid NaNO$_{3}$.

The $^{27}$Al NMR spectra of stationary samples were acquired using the Solomon echo sequence with two pulses of the same length $t_p$, separated by a delay $\tau$. For all half-integer spins with $I > 3/2$, this pulse sequence generates in general a whole series of echoes. For $^{27}$Al ($I = 5/2$), echoes at $\tau$, $2\tau$, and $3\tau$ after the second pulse are expected for the inner satellite transitions ($\pm (1/2 \pm 3/2)$ and ($-3/2 \pm 1/2$)) and at $2\tau$, $\tau$, and $3\tau/2$ for the outer satellite transitions ($\pm (3/2 \pm 5/2)$ and ($-5/2 \pm 3/2$)).[24] The echoes at $\tau$, $2\tau$, and $3\tau/2$ are referred to as forbidden echoes and those at $3\tau$ and $3\tau/2$ are referred to as allowed echoes.[35-38] Which of the various echoes are experimentally observed can to a certain extent be influenced by the phase cycling applied.[39] The echo at $\tau$, that is used here to obtain the spectra, contains the spectral information of both satellite transitions. Solomon echoes can be generated with two in-phase pulses ($p_1$, $p_2$, $\tau$, $p_3$, $\tau$, $p_4$) or two pulses in quadrature phase ($p_1$, $\pi/2$, $p_2$, $\tau$, $p_3$, $\tau$, $p_4$).[40-42] Combining both variants with phase alternation of the second pulse and CYCLOPS (Cyclically Ordered Phase Sequence)[43] yields the 16-step phase cycle that was originally proposed by Kunwar et al.[44] This phase cycle, which is known to effectively cancel spurious signals from the NMR probe,[45] was used for the acquisition of all Solomon echo data shown here.

Solomon echoes that were obtained in this way for KAIH$_{4}$ with various pulse spacings $\tau$ are shown in Figure 6. The additional echoes at $\tau/2$ and $2\tau$ can easily be discerned. The echo at $\tau/2$ is narrower than the other two since it contains only the spectral information from the wider outer satellite transition. Obviously, the forbidden echo at $3\tau/2$ is not observed under the experimental conditions chosen. This also holds true for the forbidden echo at $3\tau$. The existence of several echoes for nuclei with $I \geq 5/2$ is generally regarded as a main drawback of this technique since Fourier transform of the time signal generally leads to distorted
Figure 6. $^{27}$Al NMR Solomon echoes generated for KAlH$_4$ by applying two pulses ($t_p = 0.9 \mu$s) separated by 200, 300, 400, and 500 $\mu$s (from top to bottom). For recording these echoes, a short pre-acquisition delay of only 50 $\mu$s was used.

spectra, necessitating a direct analysis of the echoes in the time domain.\(^{[34,35]}\)

To minimize the interfering effect of the echo generated at $2\tau$ after the second pulse, we generally used pulse spacings $\tau$ of at least 0.5 ms. For both KAlH$_4$ and NaAlH$_4$, intense echoes at $\tau$ could be obtained for pulse spacings up to 1.2 ms. Since Solomon echoes can only be observed if the pulse spacing is much smaller than the duration of the free induction decay of the central transition ($T_{2\text{ff}}$),\(^{[34,35]}\) the rather slow spin-spin relaxation in these two aluminium hydrides is obviously a fortunate circumstance for the application of this technique.

For the spectra shown here, two strong rf pulses ($\nu_p \approx 100$ kHz) with a length $t_p = 0.9 \mu$s were applied. With a repetition time of 2 s, between 16,000 and 48,000 scans were accumulated. To start Fourier transform at the top of the echo at $\tau$, a pre-acquisition delay slightly shorter than $\tau$ and an appropriate number of left shifts were applied (dwell time: 0.05 $\mu$s).

The spectra simulations were performed using the solids lineshape analysis module implemented in the TopSpin 3.2 NMR software package from Bruker BioSpin GmbH.

**DFT-GIPAW Calculations**

All DFT calculations were carried out using the CASTEP code.\(^{[60,61]}\) The calculations employed the PBE exchange-correlation functional,\(^{[62]}\) using ultrasoft pseudopotentials generated on the fly and a plane wave cutoff energy of 800 eV. The structures of NaAlH$_4$ and KAlH$_4$ were optimized, relaxing all atomic positions while fixing the unit cell parameters to experimental values. The optimizations, which employed a BFGS optimizer, were considered converged when the maximal residual force on an atom fell below 0.001 eV/Å and when the maximal atomic displacement with respect to the previous step was smaller than 0.0005 Å.

The starting structure of NaAlH$_4$ was taken from the work of Hauback et al. (space group $I4_1/a$, $a = 5.0119$ Å, $c = 11.3147$ Å).\(^{[46]}\) The alternative use of the structural data published by Ozolins et al. (space group $I4_1/a$, $a = 5.0099$ Å, $c = 11.3228$ Å)\(^{[45]}\) led to essentially identical results. A $7 \times 7 \times 3$ mesh of $k$-points, corresponding to 26 irreducible points, was used to sample the first Brillouin zone. For KAlH$_4$, the atomic coordinates were taken from a previous neutron diffraction study of KAlH$_4$ by Zibrowius and Felderhoff (space group $Pnma$, $a = 8.8475$ Å, $b = 5.8143$ Å, $c = 7.3448$ Å).\(^{[26]}\) For this structure, a $4 \times 6 \times 5$ mesh of $k$-points, corresponding to 18 irreducible points, was used.

DFT calculations of the isotropic shielding parameter $\sigma_{\text{iso}}$, the quadrupole coupling constant $C_Q$, and the asymmetry parameter $\eta$ employed the gauge-including projector augmented wave (GPAW) method as implemented in the CASTEP package.\(^{[39,64-66]}\) Calculations were performed on the DFT-optimized structures, as a prior optimization of the atomic coordinates obtained from diffraction data is crucial to obtain meaningful results for hydrogen-containing systems. Even when neutron diffraction is used, a highly accurate determination of the hydrogen positions is challenging. Inaccuracies in the hydrogen positions result in large errors in the calculated NMR parameters.\(^{[39,67,68]}\) In terms of exchange-correlation functional, pseudopotentials, cutoff energy, and $k$-meshes, the same settings as for the optimizations were used for the DFT-GIPAW calculations. The analysis of the calculated NMR parameters made use of the MagResView tool.\(^{[19]}\)

In order to compare the isotropic magnetic shielding $\sigma_{\text{iso},\text{DFT}}$ directly obtained from the DFT-GIPAW computations with the experimentally accessible chemical shift data, a conversion to $\delta_{\text{iso},\text{DFT}}$ is required. In the first place, such a conversion was made by using LiAlH$_4$ as the sole reference system. Calculations analogous to those described above were carried out for LiAlH$_4$ using the crystal structure of LiAlD$_4$ reported by Hauback et al.\(^{[21]}\) as starting point ($k$-mesh: $8 \times 5 \times 5$). The chemical shift of the systems of interest was then calculated as:

$$\delta_{\text{iso},\text{DFT}} = 454.8 \text{ ppm} + 102.0 \text{ ppm} - \sigma_{\text{iso},\text{DFT}} = 556.8 \text{ ppm} - \sigma_{\text{iso},\text{DFT}}\text{ ppm}\quad (3)$$

where 454.8 ppm corresponds to the shielding value $\delta_{\text{iso},\text{DFT}}$ calculated for LiAlH$_4$, and 102.0 ppm is the isotropic shift experimentally observed with respect to the usual standard.\(^{[21]}\)

To evaluate the performance of the DFT-GIPAW computations across a broader set of systems, additional calculations were carried out for three other alkali aluminium hydrides, namely Li$_2$AlH$_4$ ($k$-mesh: $6 \times 6 \times 4$),\(^{[71]}\) Na$_2$AlH$_4$ ($k$-mesh: $6 \times 6 \times 4$),\(^{[46]}\) and K$_2$AlH$_4$ ($k$-mesh: $6 \times 6 \times 6$).\(^{[72]}\) The references cited for the structures are combined X-ray and neutron diffraction studies of the corresponding isostructural aluminium deuterides. The experimental data for $\delta_{\text{iso}}$ of Li$_2$AlH$_4$ were taken from Wiench et al.\(^{[21]}\) and those for Na$_2$AlH$_4$ and Na$_2$LiAlH$_4$ from Zhang et al.\(^{[18]}\)

It should be noted that there are no two-equivalent Al atoms in the rhombohedral crystal structure reported for Li$_2$AlH$_4$ by Brinks and Hauback.\(^{[21]}\) In particular, because of the results of a detailed analysis carried out by Levkiv et al.\(^{[73,74]}\) we regard this structural solution as rather convincing. Surprisingly, only a single resonance line was observed in the NMR spectrum of Li$_2$AlH$_4$.\(^{[77]}\) Our calculations yield a clue to explain this apparent discrepancy. For the magnetic shielding $\sigma_{\text{iso},\text{DFT}}$ of Al1 and Al2 in Li$_2$AlH$_4$, we obtained 600.2 ppm and 602.7 ppm, respectively. The results for the quadru-
The squared correlation coefficient for the solid-state phase transformation shows the direct results of the DFT-GIPAW calculations and enlarged versions of Figures 2 and 4. Furthermore, it has to be taken into account that the Li resonance lines are expected to be only 0.2 ppm apart of each other. However, the much stronger quadrupole coupling leads to a more significant second-order broadening and to a more pronounced quadrupole-induced high-field shift. At the resonance frequency of 104 MHz used by Wiench et al.,² the resolution of the X-ray powder pattern for the obtained product was insufficient to determine the space group. Figure S1 in the Supporting Information demonstrates that under these circumstances the resonance line of Al1 would be hardly visible. A high-field NMR investigation using well crystallized material should be able to verify our hypothesis.

To establish an equation to convert the shielding $\delta_{\text{iso,DFT}}$ into chemical shifts $\delta_{\text{iso,DFT}}$, a linear regression was computed across all six systems. Literature data for $\delta_{\text{iso}}$ of the two hydrides studied here, NaAlH$_4$ and KAlH$_4$, were included in the regression.²⁸ The data points as well as the linear fit are shown in Figure 7. The resulting equation for the conversion is:

$$\delta_{\text{iso,DFT}} = 514.3 \, \text{ppm} - 0.9064 \cdot \delta_{\text{iso,DFT}}.$$

### Supporting Information

The Supporting Information contains a table with the direct results of the DFT-GIPAW calculations ($C_{\text{CR}}, \eta, \sigma_i$) for all six aluminium hydrides mentioned in the paper, a figure with the simulated $^{27}$Al MAS NMR spectrum of Li$_2$AlH$_6$ at a resonance frequency of 104 MHz based on the parameters from the DFT-GIPAW calculations and enlarged versions of Figures 2 and 4.

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### Conflict of Interest

There are no conflicts to declare.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

density functional calculations · hydrogen storage materials · materials science · metal hydrides · solid-state NMR spectroscopy
