Nuclear Magnetic Resonance Study of Anion and Cation Dynamics in CsSiH$_3$

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Abstract

In order to study the dynamical properties of cesium silanide CsSiH₃, we have measured the ¹H and ¹³³Cs nuclear magnetic resonance (NMR) spectra and spin-lattice relaxation rates in this compound over the temperature range of 5 K to 354 K. The results of the ¹H NMR measurements indicate that [SiH₃]⁻ anions in CsSiH₃ retain unusually high reorientational mobility down to low temperatures. In particular, a significant narrowing of the proton NMR spectrum due to [SiH₃]⁻ reorientations is observed in the range of 10 K to 14 K. The order-disorder (β→α) phase transition accompanied by the strong acceleration of [SiH₃]⁻ reorientations is observed above 200 K; according to the ¹H spin-lattice relaxation data, this transition appears to be gradual. For the high-temperature disordered α-phase, the activation energy for [SiH₃]⁻ reorientations is found to be 41(4) meV. The ¹³³Cs NMR results are consistent with the onset of diffusive motion of Cs⁺ cations at the frequency scale of ≈10⁴ s⁻¹ above 300 K.

Keywords: A. Energy storage materials; C. Diffusion; D. Nuclear resonances
1. Introduction

Alkali-metal silanides \( M \text{SiH}_3 \) \((M = \text{K}, \text{Rb}, \text{Cs})\) consisting of \( M^+ \) cations and pyramidal \([\text{SiH}_3]^–\) anions have received significant recent attention as potential hydrogen-storage materials [1-5]. These compounds can be prepared by reversible hydrogenation of Zintl phases \( M\text{Si} \) with the equilibrium hydrogen gas pressure of 0.1 MPa near 410 K [3]. Above 300 K, the crystal structure of all three \( M\text{SiH}_3 \) compounds is cubic (\( \alpha \)-phase, space group \( Fm\overline{3}m \)) with NaCl-type arrangement of \( M^+ \) cations and orientationally disordered \([\text{SiH}_3]^–\) anions. At lower temperatures, these disordered \( \alpha \)-phases are transformed into the ordered \( \beta \)-phases with orthorhombic (\( \beta \)-K\text{SiH}_3, space group \( Pnma \)) or monoclinic (\( \beta \)-Rb\text{SiH}_3 and \( \beta \)-Cs\text{SiH}_3, space group \( P2_1/m \)) structures [3,6,7]. The corresponding entropy-driven \( \alpha \leftrightarrow \beta \) phase transitions are found to be reversible, but hysteretic [7,8].

It is known that in many complex hydrides, the reorientational motion of complex anions (such as \([\text{BH}_4]^–\), \([\text{AlH}_4]^–\), \([\text{NH}_2]^–\), \([\text{B}_{12}\text{H}_{12}]^2–\)) [9-13] strongly contributes to the balance of energies determining the thermodynamic stability of these compounds; therefore, information on the anion reorientational dynamics is important for understanding the fundamental properties of complex hydrides. The first evidence of the reorientational motion of \([\text{SiH}_3]^–\) anions in alkali-metal silanides was obtained in the wide-line nuclear magnetic resonance (NMR) study [14] that revealed the narrowing of the \(^1\text{H} \) NMR spectrum of K\text{SiH}_3 above 170 K. The motional narrowing of the \(^2\text{D} \) NMR spectrum was also observed for deuterium-substituted K\text{SiD}_3 and Rb\text{SiD}_3 above 200 K [8]. Recent quasielastic neutron scattering (QENS) measurements [7,8,15,16] have shown that phase transitions from the ordered \( \beta \)-phases of \( M\text{SiH}_3 \) to the disordered \( \alpha \)-phases are accompanied by the strong acceleration of anion reorientations. Typical reorientational jump rates for \( \alpha \)-phases of all \( M\text{SiH}_3 \) compounds just above room temperature are of the order of \( 10^{12} \) s\(^{-1}\). It is interesting to note that similar order-disorder phase transitions accompanied by an acceleration of anion reorientations have been found to occur in a number of complex hydrides, including the family of alkali-metal \textit{closo}-hydroborates with \([\text{B}_{12}\text{H}_{12}]^2–\) and \([\text{B}_{10}\text{H}_{10}]^2–\) anions [13,17-19]. The high-temperature disordered phases of lithium and sodium \textit{closo}-hydroborates and their derivatives exhibit extremely high Li\(^+\) and Na\(^+\) ionic conductivities [19-21], which are believed to be related [22-24] to fast anion reorientations. For alkali-metal
silanides, a possible relation between anion reorientations and cation diffusion has not been studied so far.

In the present work, we use nuclear magnetic resonance measurements of $^1$H and $^{133}$Cs spectra and spin-lattice relaxation rates to investigate both the reorientational motion of [SiH$_3$]$^-$ anions and the diffusive motion of Cs$^+$ cations in CsSiH$_3$ over wide temperature ranges. The results of this first NMR study of CsSiH$_3$ indicate that [SiH$_3$]$^-$ reorientations in $\beta$-CsSiH$_3$ are unusually fast, and on the frequency scale of $10^5$ s$^{-1}$ they are not “frozen out” down to very low temperatures. The diffusive motion of Cs$^+$ cations becomes observable at the NMR frequency scale in $\alpha$-CsSiH$_3$ above 300 K.

2. Experimental details

CsSiH$_3$ sample was prepared by the direct solid – gas reaction between CsSi and H$_2$, as described in Ref. [3]. The Zintl phase CsSi was synthesized by high-temperature annealing of a 1:1.03 mixture of cesium (99.8%, Alfa Aesar [25]) and silicon (powder, -325 mesh, Sigma Aldrich). All materials were handled in an argon-filled glovebox. The mixture was arc-weld-sealed within a stainless-steel ampule inside the glovebox. The ampule was heated to 873 K and kept at this temperature for 48 h. Then it was cooled with the rate of 0.2 K/min down to room temperature. A slight excess of silicon was added to ensure a complete reaction of the starting cesium. The resulting CsSi compound was first activated via evacuation at 473 K for 12 h and then hydrogenated at 373 K with 5 MPa of hydrogen for 24 h. For NMR experiments, the powdered CsSiH$_3$ sample was flame-sealed in a glass tube under 0.5 bar of nitrogen gas.

Low-field $^1$H NMR measurements were performed on a pulse spectrometer with quadrature phase detection at the frequencies $\omega/2\pi = 28$ and 90 MHz. The magnetic field was provided by a 2.1 T iron-core Bruker magnet. A home-built multinuclear continuous-wave NMR magnetometer working in the range 0.32 T to 2.15 T was used for field stabilization. For rf pulse generation, we used a home-built computer-controlled pulse programmer, a PTS frequency synthesizer (Programmed Test Sources, Inc.) and a 1 kW Kalmus wideband pulse amplifier. A probehead with the sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using nitrogen or helium as a cooling agent. The sample temperature monitored by a chromel – (Au-Fe) thermocouple was stable to ±0.1 K. High-field $^{133}$Cs NMR measurements
were performed on a Bruker AVANCE III 500 spectrometer at the frequency $\omega/2\pi = 65.62$ MHz. Typical values of the $\pi/2$ pulse length were 3 $\mu$s to 4 $\mu$s for both $^1$H and $^{133}$Cs. All the NMR measurements were performed with increasing temperature and with 15 minutes stabilization time at each temperature prior to a measurement. Nuclear spin-lattice relaxation rates were measured using the saturation – recovery method. NMR spectra were recorded by Fourier transforming the solid echo signals (pulse sequence $\pi/2 - t - \pi/2$).

3. Results and discussion

3.1. $^1$H NMR spectra and spin-lattice relaxation rates

The evolution of the proton NMR spectra for CsSiH$_3$ with temperature is shown in Fig. 1. As can be seen from this figure, the spectra exhibit a considerable narrowing with increasing temperature. Figure 2 shows the temperature dependence of the line width $\Delta_H$ (full width at half-maximum). At low temperatures, the width of the $^1$H NMR spectrum is determined by dipole-dipole interactions between static nuclear spins; this is the ‘rigid-lattice’ line width $\Delta_{HR}$. A rough theoretical estimate of $\Delta_{HR}$ can be obtained from the second moment calculations using the structural data for $\beta$-CsSiH$_3$ [3], see Fig. 3. The calculated ‘rigid-lattice’ second moment of the $^1$H NMR line for $\beta$-CsSiH$_3$ is $5.2 \times 10^9$ s$^{-2}$. Assuming a Gaussian shape of the spectrum, this second moment should correspond to the $\Delta_{HR}$ value of 27.1 kHz. The experimental $\Delta_H$ value at $T = 5$ K (28.8 kHz) is close to this estimate.

With increasing temperature, the line width starts to decrease, since the onset of H jump motion leads to a partial averaging of dipole-dipole interactions. Such motional narrowing is expected to be substantial at the temperature at which the H jump rate $\tau^{-1}$ becomes nearly equal to $2\pi \Delta_{HR}$ [26]; for $\beta$-CsSiH$_3$, this characteristic frequency is about $1.7 \times 10^5$ s$^{-1}$. As can be seen from Fig. 2, a considerable line narrowing in $\beta$-CsSiH$_3$ is observed already at 14 K. This means that SiH$_3$ groups in the cesium silanide retain high reorientational mobility down to very low temperatures. For comparison, the onset of the proton NMR line narrowing in $\beta$-KSiH$_3$ occurs near 170 K [14]. Recent QENS studies of $M$SiH$_3$ compounds [16] have shown that the reorientational SiH$_3$ motion in $\beta$-CsSiH$_3$ is much faster than in $\beta$-KSiH$_3$ and $\beta$-RbSiH$_3$. However, because of the limited energy resolution of QENS measurements, they can only probe the jump
rates down to \( \approx 4 \times 10^8 \text{ s}^{-1} \) (for \( \beta \)-CsSiH\(_3\), this low limit corresponds to the temperature of about 140 K [16]). Since NMR measurements are sensitive to much slower jump rates, they allow us to trace the reorientational motion down to lower temperatures. An Arrhenius extrapolation of the QENS results for \( \beta \)-CsSiH\(_3\) [16] to the low-\( T \) region indicates that the H jump rate of \( 10^5 \text{ s}^{-1} \) is expected to occur near 73 K. Thus, SiH\(_3\) reorientations are not “frozen out” at the frequency scale of \( 10^5 \text{ s}^{-1} \) down to much lower temperatures than those expected on the basis of extrapolation of the QENS data.

As can be seen from Fig. 2, in the temperature range of 100 K to 200 K, the value of \( \Delta_H \) remains nearly constant. This plateau regime is related to the fact that even in the case of \( \tau^{-1} \) largely higher than \( 2\pi \Delta_{HR} \), a localized H motion (such as reorientational motion) leads to only partial averaging of the dipole-dipole interactions. The plateau value of \( \Delta_H \) should depend on the mechanism of reorientations. For \( \beta \)-CsSiH\(_3\), the second moment of the proton NMR line is dominated by \(^1\text{H} - ^1\text{H} \) interactions within the same SiH\(_3\) group (the ‘intramolecular’ contribution). A fast uniaxial rotation of SiH\(_3\) group around the 3-fold symmetry axis is expected to result in a 75 % drop of this contribution to the second moment with respect to its ‘rigid-lattice’ value [14,27]. Assuming that the line shape is Gaussian, this corresponds to a 50 % drop of the line width. The experimental plateau value of \( \Delta_H \) for \( \beta \)-CsSiH\(_3\) (\( \approx 15 \text{ kHz} \)) is indeed close to one-half of the low-temperature value; this is consistent with the model of uniaxial reorientations, in agreement with the QENS results for \( \beta \)-phases of MSiH\(_3\) [16]. The additional decrease in the line width above 220 K (Fig. 2) can be attributed to the change in the reorientational mechanism related to the \( \beta \rightarrow \alpha \) phase transition [16]. QENS data for the orientationally-disordered \( \alpha \)-phases of MSiH\(_3\) [7,15,16] are consistent with the reorientational mechanism in which each H atom traverses many sites on the surface of a sphere roughly centered on the Si atom. The effects of such nearly isotropic reorientational motion on \( \Delta_H \) can be estimated in the following way. Since fast isotropic rotations should average out the dipole-dipole interactions within SiH\(_3\) groups, we have to calculate only the ‘intermolecular’ contribution to the second moment (between different SiH\(_3\) groups and between SiH\(_3\) groups and \(^{133}\text{Cs} \) spins). This contribution can be roughly estimated by placing all protons in each SiH\(_3\) group to its center (Si atom) and taking into account only the distances between centers of different groups [10]. The second moment for \( \alpha \)-CsSiH\(_3\) calculated using this approach is \( 4.1 \times 10^8 \text{ s}^{-2} \); for a Gaussian shape of the proton NMR line, this value corresponds to the line width of
7.6 kHz. The experimental value of Δ_H at the high-temperature end of our measurements (8.2 kHz) is close to this estimated level.

The behavior of the proton spin-lattice relaxation rates R'' measured at two resonance frequencies (ω/2π = 28 and 90 MHz) is shown in Fig. 4. General features of the observed temperature dependence of R'' are typical of complex hydrides with reorienting anions [9], where the dominant relaxation mechanism is related to motional modulation of the dipole-dipole interaction between nuclear spins. For this mechanism, the proton spin-lattice relaxation rate exhibits a peak at the temperature at which the reorientational jump rate τ⁻¹ becomes nearly equal to the nuclear magnetic resonance frequency ω. According to the standard theory [26], in the limit of slow motion (ωτ ≫ 1), R'' is proportional to ω⁻²τ⁻¹, and in the limit of fast motion (ωτ ≪ 1), R'' is proportional to τ being frequency-independent. If the temperature dependence of the jump rate τ⁻¹ follows the Arrhenius law with the activation energy E_a,

\[ \tau^{-1} = \tau_0^{-1} \exp\left(-\frac{E_a}{k_B}\right), \]  

(1)
a plot of ln R'' versus T⁻¹ is expected to be linear in the limits of both slow and fast motion with the slopes of E_a/k_B and E_a/k_B, respectively. As can be seen from Fig. 4, the observed behavior of R'' for CsSiH₃ strongly deviates from that predicted by the standard theory. First, the high-temperature slope of the ln R'' vs. T⁻¹ peak appears to be much steeper than the low-temperature one. Second, the observed frequency dependence of R'' at the low-temperature slope is considerably weaker than the predicted ω⁻² dependence. Furthermore, there are certain deviations from the linear behavior of the ln R'' vs. T⁻¹ plot both at high and low temperatures. The most evident reason for the unusual behavior of the proton spin-lattice relaxation rate in CsSiH₃ is the β → α phase transition accompanied by the strong acceleration of the reorientational motion of SiH₃ groups. Because of this phase transition, the steep high-temperature slope of the R''(T) peak cannot be described in terms of regular thermally-activated changes in τ⁻¹; this slope should reflect rapid changes in the H jump rate due to the phase change. It is interesting to note that in some complex hydrides the order-disorder phase transitions lead to abrupt changes in R''; for example, the order-disorder transition in sodium closo-hydroborate Na₂B₁₂H₁₂ near 520 K is
accompanied by the two-orders-of-magnitude drop of $R_i^{iH}$ over the temperature interval of 5 K [13]. For CsSiH$_3$, the relaxation rate drop is not so sharp; this may be related to specific features of the $\beta - \alpha$ phase transitions in MSiH$_3$ occurring via intermediate phases [8,16]. The presence of disordered $\alpha$-like nanodomains at temperatures much lower than the phase transition points was first reported for KSiH$_3$ and RbSiH$_3$ [8]. Because of their small size (2 nm to 4 nm [8]), these nanodomains may be invisible in diffraction experiments. The comprehensive QENS results for CsSiH$_3$ [16] are consistent with the presence of a nanostructured intermediate phase ($i$-phase) with the distinct reorientational dynamics being much faster than that for the $\beta$-phase, but slower than that for the $\alpha$-phase. According to the QENS data [16], the $\alpha$-, $i$-, and $\beta$-phases in CsSiH$_3$ can coexist over the temperature range of at least 170 K to 250 K.

The complex behavior of CsSiH$_3$ related to the order-disorder phase transition prevents us from any attempts to parametrize the $R_i^{iH}(T)$ data over the entire temperature range studied. Therefore, we have only tried to parametrize the $R_i^{iH}(T)$ data at low temperatures ($T < 200$ K), where the $\beta$-phase is expected to be the dominant one. As noted above, the observed frequency dependence of the proton spin-lattice relaxation rate at the low-$T$ slope of the $R_i^{iH}(T)$ peak is considerably weaker than the $\omega^{-2}$ dependence. This feature is consistent with the presence of a certain distribution of H jump rates [28]. For parametrization of our low-temperature $R_i^{iH}(T)$ data, we have used the simplest model based on a Gaussian distribution of the activation energies [28]; for this model, the observed relaxation rate is expressed as

$$R_i^{iH} = \int R_i^{iH}(E_a)G(E_a,E_a,\Delta E_a)dE_a \quad .$$

(2)

Here $G(E_a,E_a,\Delta E_a)$ is a Gaussian distribution function centered on $E_a$ with the dispersion $\Delta E_a$, and $R_i^{iH}(E_a)$ is determined by combining the standard expression that relates the relaxation rate and $\tau$,

$$R_i^{iH}(E_a) = \frac{2\Delta M_{HH} \tau}{3} \left[ \frac{1}{1 + \omega^2 \tau^2} + \frac{4}{1 + 4\omega^2 \tau^2} \right] ,$$

(3)
and the Arrhenius law (Eq. (1)). The parameters of the model are the average activation energy $E_a$, the dispersion $\Delta E_a$, the pre-exponential factor $\tau_0$ and the amplitude factor $\Delta M_{HH}$ determined by the strength of the fluctuating part of dipole-dipole interaction between protons. The contribution of dipole-dipole $^1\text{H} - ^{133}\text{Cs}$ interactions to the proton relaxation rate in CsSiH$_3$ can be neglected, since these interactions give only 2.6 % of the total calculated ‘rigid-lattice’ second moment of the $^1\text{H}$ NMR line. The model parameters have been varied to find the best fit between the model $R_i^{HH}(T)$ and the experimental data for $T < 200$ K at two resonance frequencies simultaneously. The results of such a simultaneous fit are shown by the solid curves in Fig. 4; the corresponding fit parameters: $E_a = 226 \ (8)$ meV, $\Delta E_a = 78 \ (4)$ meV, $\tau_0 = 3.7(5) \times 10^{-15}$ s, and $\Delta M_{HH} = 3.4(1) \times 10^9$ s$^{-2}$. Note that the resulting fluctuating part of the second moment, $\Delta M_{HH}$, corresponds to $\approx 65$ % of the calculated ‘rigid-lattice’ second moment (see above); this is close to the expected ‘intramolecular’ value (75 %) [14,27] for the case of uniaxial rotation of SiH$_3$ groups around the 3-fold symmetry axis.

The distribution width $\Delta E_a$ resulting from the fit appears to be rather large (about one-third of $E_a$). This feature may indicate the presence of an additional jump process not resolved in the spin-lattice relaxation measurements. Indeed, if the difference between two frequency scales of H jump motion is relatively small (about one order of magnitude), an additional jump process may contribute only to the low-temperature slope of the single-peak $R_i^{HH}(T)$ dependence that mimics the typical behavior for the model with a continuous jump rate distribution. Similar behavior of $R_i^{HH}(T)$ was reported for a number of systems with two frequency scales of H jump motion, including some Laves-phase hydrides [29] and the ordered closo-hydroborate salt Rb$_2$B$_{10}$H$_{10}$ [30]. The presence of an additional jump process in the temperature range, where the $\beta$-phase is expected to be the dominant one, is also consistent with recent QENS results for CsSiH$_3$ [16]. These results indicate that the description of the elastic incoherent structure factor measured on the backscattering neutron spectrometer at 200 K in terms of the model of 3-fold SiH$_3$ reorientations (the only physically reasonable model for the ordered $\beta$-phase) requires an extra contribution (43 %) to the elastic peak intensity. Such a large extra contribution to the elastic peak intensity is consistent [16] with the presence of H atoms moving much faster than those in the $\beta$-phase.
The observed change in the high-temperature slope of the $\ln R_i^H$ vs. $T^{-1}$ plot near 300 K (see Fig. 4) can be attributed to the upper boundary of the phase transition region. This interpretation implies the existence of a single $\alpha$-phase of CsSiH$_3$ above 300 K, so that the behavior of $R_i^H$ at $T > 300$ K should be governed by the regular Arrhenius temperature dependence of $\tau$. The activation energy for H jump motion in this temperature range can be directly estimated from the proton spin-lattice relaxation data, since in the limit of fast motion (see above) $R_i^H$ is proportional to $\tau$. The estimate based on an Arrhenius approximation of our $R_i^H(T)$ data in the range 324 K to 354 K gives the activation energy of 41(4) meV. This value is close to the activation energy for $\alpha$-phase of CsSiH$_3$ (48(2) meV) found from QENS experiments [16].

3.2. $^{133}$Cs NMR spectra and spin-lattice relaxation rates

The evolution of the $^{133}$Cs NMR spectra for CsSiH$_3$ with temperature is shown in Fig. 5. As in the case of the proton NMR spectra, with increasing temperature we observe a considerable narrowing of the $^{133}$Cs spectra accompanied by changes in their shape. The temperature dependence of the $^{133}$Cs NMR line width $\Delta_{Cs}$ (full width at half-maximum) is shown in Fig. 6. In the studied temperature range of 120 – 350 K, the most pronounced drop of $\Delta_{Cs}$ is observed between 260 K and 300 K, and at $T > 300$ K, the line width reaches a plateau. Such a behavior is typical of the case of diffusing cations in ionic conductors (see, for example, the “steps” in $^7$Li NMR line widths in Refs. [31-33]). It should be noted, however, that in our case we should distinguish between the effects due to the reorientational H motion and the diffusive motion of Cs$^+$ cations. For this purpose, we can use the results of the $^{133}$Cs spin-lattice relaxation rate measurements shown in Fig. 7.

Comparison of Figs. 7 and 4 indicates that below 300 K, the behavior of the $^{133}$Cs spin-lattice relaxation rate, $R_i^{Cs}$, resembles that of $R_i^H$. In particular, the $R_i^{Cs}(T)$ peak is observed at nearly the same temperature as the $R_i^H(T)$ peak. Thus, the observed $^{133}$Cs relaxation rate peak can be attributed to the reorientational motion of SiH$_3$ groups that modulates the relatively weak $^{133}$Cs – $^1$H dipole-dipole interaction. This is supported by the small amplitude of the $R_i^{Cs}(T)$ peak (0.36 s$^{-1}$) which is two orders of magnitude lower than the amplitude of the $R_i^H(T)$ peak. Such a
difference in the maximum values of the spin-lattice relaxation rates is in general agreement with
the estimated contributions of $^{133}\text{Cs} - ^1\text{H}$ and $^1\text{H} - ^1\text{H}$ dipole-dipole interactions to the
corresponding second moments. It should be noted that reorientational jumps of SiH$_3$ groups are
not expected to add any electric quadrupole contribution to the $^{133}\text{Cs}$ relaxation rate, since each
reorientational jump does not change the charge configuration around Cs sites. In contrast to the
case of the electric quadrupole interaction, the dipole-dipole interaction is pairwise, i.e., any
changes in the radius vector connecting a pair of interacting nuclear spins should contribute to
the nuclear spin relaxation. It can be concluded that the behavior of the $^{133}\text{Cs}$ spin-lattice
relaxation rate below 300 K is governed by the reorientational motion of SiH$_3$ groups via $^{133}\text{Cs} - ^1\text{H}$ dipole-dipole interactions.

Above 300 K, the $^{133}\text{Cs}$ relaxation rate starts to increase with increasing temperature (Fig. 7). This behavior of $R'_1^{\text{Cs}}$ differs qualitatively from that of $R''_1$ in the same temperature range (Fig. 4); it is consistent with the onset of an additional low-frequency jump process, such as
diffusive jumps of Cs$^+$ ions. It should be noted that $R'_1^{\text{Cs}}$ starts to increase at temperatures just
above the characteristic “step” in the line width $\Delta_{\text{Cs}}$ (Fig. 6). This feature is typical of the onset
of cation diffusive motion on the NMR frequency scale [31-33]; it corresponds to the case when
the cation jump rate is higher than $\approx 10^4$ s$^{-1}$ (sufficient to cause the NMR line narrowing), but is
still considerably lower than $\approx 10^8$ s$^{-1}$ (not reaching a new relaxation rate maximum).

5. Conclusions

The results of our proton NMR measurements indicate that [SiH$_3$]$^-\text{ groups in CsSiH}_3$
retain unusually high reorientational mobility down to low temperatures. According to the $^1\text{H}$
NMR line width measurements, even at $T = 14$ K the jump rate of SiH$_3$ reorientations in CsSiH$_3$
is about $10^5$ s$^{-1}$. In agreement with recent QENS results for CsSiH$_3$ [16], our proton spin-lattice
relaxation data are consistent with a coexistence of at least two reorientational jump processes
below 200 K. The order-disorder ($\beta\rightarrow\alpha$) phase transition accompanied by the strong acceleration
of SiH$_3$ reorientations leads to the considerable drop of the measured $^1\text{H}$ spin-lattice relaxation
rate $R''_1$; however, this drop is not as abrupt as in the case of the order-disorder transitions in
borohydrides [34] and closo-hydroborates [13]. The smearing of the $R''_1$ “step” in the phase

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transition region for CsSiH$_3$ suggests that the order-disorder transition in this compound occurs via the formation of an intermediate phase [16]. For the high-temperature disordered $\alpha$-phase of CsSiH$_3$, the activation energy for SiH$_3$ reorientations estimated from our $R_{1H}^\prime(T)$ data is 41(4) meV. The $^{133}$Cs NMR results are consistent with the onset of diffusive motion of Cs$^+$ ions at the frequency scale of $\approx 10^4$ s$^{-1}$ above 300 K.

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[25] The mention of all commercial suppliers in this paper is for clarity and does not imply the recommendation or endorsement of these suppliers by NIST.


**Fig. 1.** Evolution of the proton NMR spectrum for CsSiH$_3$ with temperature.

**Fig. 2.** Temperature dependence of the width (full width at half-maximum) of the $^1$H NMR spectrum measured for CsSiH$_3$ at 28 MHz.
Fig. 3. Schematic view of the structure of $\beta$-CsSiH$_3$ (along the $c$ axis). Olive spheres: Cs atoms; gray spheres: Si atoms; blue spheres: H atoms.

Fig. 4. Proton spin-lattice relaxation rates measured at 28 MHz and 90 MHz for CsSiH$_3$ as functions of the inverse temperature. The solid lines show the simultaneous fit of the model with a Gaussian distribution of the activation energies to the data in the range 80 K to 200 K.
Fig. 5. Evolution of the $^{133}$Cs NMR spectrum for CsSiH$_3$ with temperature.

Fig. 6. Temperature dependence of the width (full width at half-maximum) of the $^{133}$Cs NMR spectrum measured for CsSiH$_3$ at 65.62 MHz.
Fig. 7. $^{133}$Cs spin-lattice relaxation rate measured at 65.62 MHz for CsSiH$_3$ as a function of the inverse temperature.