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# **Nuclear magnetic resonance study of anion and cation dynamics in CsSiH<sub>3</sub>**

R.V. Skoryunov<sup>1</sup>, O.A. Babanova<sup>1</sup>, A.V. Soloninin<sup>1</sup>, A.V. Skripov<sup>1,\*</sup>,  
J.-N. Chotard<sup>2</sup>, R. Janot<sup>2</sup>, W.S. Tang<sup>3,4,5</sup>, M. Dimitrievska<sup>3,6</sup>,  
T.J. Udovic<sup>3</sup>

<sup>1</sup> *Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences,  
Ekaterinburg 620108, Russia*

<sup>2</sup> *Laboratoire de Réactivité et Chimie des Solides (LRCS), UMR 7314 CNRS,  
Université de Picardie Jules Verne, 80039 Amiens Cedex, France*

<sup>3</sup> *NIST Center for Neutron Research, National Institute of Standards and Technology,  
Gaithersburg, MD 20899-6102, USA*

<sup>4</sup> *Department of Materials Science and Engineering, University of Maryland,  
College Park, MD 20742-2115, USA*

<sup>5</sup> *Geophysical Laboratory, Carnegie Institution of Washington, Washington,  
DC 20015, USA*

<sup>6</sup> *National Renewable Energy Laboratory, Golden, CO 80401, USA*

\* Corresponding author. E-mail: [skripov@imp.uran.ru](mailto:skripov@imp.uran.ru) Telephone: +7-343-378-3781

## Abstract

In order to study the dynamical properties of cesium silanide  $\text{CsSiH}_3$ , we have measured the  $^1\text{H}$  and  $^{133}\text{Cs}$  nuclear magnetic resonance (NMR) spectra and spin-lattice relaxation rates in this compound over the temperature range of 5 – 354 K. The results of the  $^1\text{H}$  NMR measurements indicate that  $[\text{SiH}_3]^-$  anions in  $\text{CsSiH}_3$  retain unusually high reorientational mobility down to low temperatures. In particular, a significant narrowing of the proton NMR spectrum due to  $[\text{SiH}_3]^-$  reorientations is observed in the range  $\sim 10 - 14$  K. The order-disorder ( $\beta \rightarrow \alpha$ ) phase transition accompanied by the strong acceleration of  $[\text{SiH}_3]^-$  reorientations is observed above 200 K; according to the  $^1\text{H}$  spin-lattice relaxation data, this transition appears to be gradual. For the high-temperature disordered  $\alpha$ -phase, the activation energy for  $[\text{SiH}_3]^-$  reorientations is found to be 41(4) meV. The  $^{133}\text{Cs}$  NMR results are consistent with the onset of diffusive motion of  $\text{Cs}^+$  cations at the frequency scale of  $\sim 10^4 \text{ s}^{-1}$  above 300 K.

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

## 1. Introduction

Alkali-metal silanides  $MSiH_3$  ( $M = K, Rb, Cs$ ) consisting of  $M^+$  cations and pyramidal  $[SiH_3]^-$  anions have received significant recent attention as potential hydrogen-storage materials [1-5]. These compounds can be prepared by reversible hydrogenation of Zintl phases  $MSi$  with the equilibrium hydrogen gas pressure of 0.1 MPa near 410 K [3]. Above 300 K, the crystal structure of all three  $MSiH_3$  compounds is cubic ( $\alpha$ -phase, space group  $Fm\bar{3}m$ ) with NaCl-type arrangement of  $M^+$  cations and orientationally disordered  $[SiH_3]^-$  anions. At lower temperatures, these disordered  $\alpha$ -phases are transformed into the ordered  $\beta$ -phases with orthorhombic ( $\beta$ - $KSiH_3$ , space group  $Pnma$ ) or monoclinic ( $\beta$ - $RbSiH_3$  and  $\beta$ - $CsSiH_3$ , 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  $[BH_4]^-$ ,  $[AlH_4]^-$ ,  $[NH_2]^-$ ,  $[B_{12}H_{12}]^{2-}$ ) [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  $[SiH_3]^-$  anions in alkali-metal silanides was obtained in the wide-line nuclear magnetic resonance (NMR) study [14] that revealed the narrowing of the  $^1H$  NMR spectrum of  $KSiH_3$  above 170 K. The motional narrowing of the  $^2D$  NMR spectrum was also observed for deuterium-substituted  $KSiD_3$  and  $RbSiD_3$  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  $MSiH_3$  to the disordered  $\alpha$ -phases are accompanied by the strong acceleration of anion reorientations. Typical reorientational jump rates for  $\alpha$ -phases of all  $MSiH_3$  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 *closo*-borates with  $[B_{12}H_{12}]^{2-}$  and  $[B_{10}H_{10}]^{2-}$  anions [13,17-19]. The high-temperature disordered phases of lithium and sodium *closo*-borates 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  $^1\text{H}$  and  $^{133}\text{Cs}$  spectra and spin-lattice relaxation rates to investigate both the reorientational motion of  $[\text{SiH}_3]^-$  anions and the diffusive motion of  $\text{Cs}^+$  cations in  $\text{CsSiH}_3$  over wide temperature ranges. The results of this first NMR study of  $\text{CsSiH}_3$  indicate that  $[\text{SiH}_3]^-$  reorientations in  $\beta$ - $\text{CsSiH}_3$  are unusually fast, and on the frequency scale of  $10^5 \text{ s}^{-1}$  they are not “frozen out” down to very low temperatures. The diffusive motion of  $\text{Cs}^+$  cations becomes observable at the NMR frequency scale in  $\alpha$ - $\text{CsSiH}_3$  above 300 K.

## 2. Experimental details

$\text{CsSiH}_3$  sample was prepared by the direct solid – gas reaction between  $\text{CsSi}$  and  $\text{H}_2$ , as described in Ref. [3]. The Zintl phase  $\text{CsSi}$  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  $\text{CsSi}$  compound was first activated via evacuation at 473 K for 12 h and then hydrogenated at 373 K with  $\sim 5$  MPa of hydrogen for 24 h. For NMR experiments, the powdered  $\text{CsSiH}_3$  sample was flame-sealed in a glass tube under  $\sim 0.5$  bar of nitrogen gas.

Low-field  $^1\text{H}$  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 – 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  $\pm 0.1$  K. High-field  $^{133}\text{Cs}$  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 – 4  $\mu\text{s}$  for both  $^1\text{H}$  and  $^{133}\text{Cs}$ . 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  $\pi/2_x - t - \pi/2_y$ ).

### 3. Results and discussion

#### 3.1. $^1\text{H}$ NMR spectra and spin-lattice relaxation rates

The evolution of the proton NMR spectra for  $\text{CsSiH}_3$  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  $\Delta_{\text{H}}$  (full width at half-maximum). At low temperatures, the width of the  $^1\text{H}$  NMR spectrum is determined by dipole-dipole interactions between static nuclear spins; this is the ‘rigid-lattice’ line width  $\Delta_{\text{HR}}$ . A rough theoretical estimate of  $\Delta_{\text{HR}}$  can be obtained from the second moment calculations using the structural data for  $\beta\text{-CsSiH}_3$  [3], see Fig. 3. The calculated ‘rigid-lattice’ second moment of the  $^1\text{H}$  NMR line for  $\beta\text{-CsSiH}_3$  is  $5.2 \times 10^9 \text{ s}^{-2}$ . Assuming a Gaussian shape of the spectrum, this second moment should correspond to the  $\Delta_{\text{HR}}$  value of 27.1 kHz. The experimental  $\Delta_{\text{H}}$  value at  $T = 5 \text{ K}$  (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  $2\pi\Delta_{\text{HR}}$  [26]; for  $\beta\text{-CsSiH}_3$ , this characteristic frequency is about  $1.7 \times 10^5 \text{ s}^{-1}$ . As can be seen from Fig. 2, a considerable line narrowing in  $\beta\text{-CsSiH}_3$  is observed already at 14 K. This means that  $\text{SiH}_3$  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  $\beta\text{-KSiH}_3$  occurs near 170 K [14]. Recent QENS studies of  $M\text{SiH}_3$  compounds [16] have shown that the reorientational  $\text{SiH}_3$  motion in  $\beta\text{-CsSiH}_3$  is much faster than in  $\beta\text{-KSiH}_3$  and  $\beta\text{-RbSiH}_3$ . However, because of the limited energy resolution of QENS measurements, they can only probe the jump rates down to  $\sim 4 \times 10^8 \text{ s}^{-1}$  (for  $\beta\text{-CsSiH}_3$ , 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  $\beta\text{-CsSiH}_3$  [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,  $\text{SiH}_3$  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 – 200 K, the value of  $\Delta_H$  remains nearly constant. This plateau regime is related to the fact that even in the case of  $\tau^{-1} \gg$  [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<sub>3</sub>, the second moment of the proton NMR line is dominated by  $^1\text{H} - ^1\text{H}$  interactions within the same SiH<sub>3</sub> group (the ‘intramolecular’ contribution). A fast uniaxial rotation of SiH<sub>3</sub> 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<sub>3</sub> (~ 15 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<sub>3</sub> [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<sub>3</sub> [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<sub>3</sub> groups, we have to calculate only the ‘intermolecular’ contribution to the second moment (between different SiH<sub>3</sub> groups and between SiH<sub>3</sub> groups and  $^{133}\text{Cs}$  spins). This contribution can be roughly estimated by placing all protons in each SiH<sub>3</sub> 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<sub>3</sub> 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  $\Delta_H$  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  $R_1^H$  measured at two resonance frequencies ( $\omega/2\pi = 28$  and 90 MHz) is shown in Fig. 34. General features of the observed temperature dependence of  $R_1^H$  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  $\tau^{-1}$  becomes nearly equal to the nuclear magnetic resonance frequency  $\omega$ . According to the standard theory [26], in the limit of slow motion ( $\omega\tau \gg 1$ ),  $R_1^H$  is proportional to  $\omega^{-2}\tau^{-1}$ , and in the limit of fast motion ( $\omega\tau \ll 1$ ),  $R_1^H$  is proportional to  $\tau$  being frequency-independent. If the temperature dependence of the jump rate  $\tau^{-1}$  follows the Arrhenius law with the activation energy  $E_a$ ,

$$\tau^{-1} = \tau_0^{-1} \exp(-E_a/k_B), \quad (1)$$

a plot of  $\ln R_1^H$  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. 34, the observed behavior of  $R_1^H$  for CsSiH<sub>3</sub> strongly deviates from that predicted by the standard theory. First, the high-temperature slope of the  $\ln R_1^H$  vs.  $T^{-1}$  peak appears to be much steeper than the low-temperature one. Second, the observed frequency dependence of  $R_1^H$  at the low-temperature slope is considerably weaker than the predicted  $\omega^{-2}$  dependence. Furthermore, there are certain deviations from the linear behavior of the  $\ln R_1^H$  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 CsSiH<sub>3</sub> is the  $\beta \rightarrow \alpha$  phase transition accompanied by the strong acceleration of the reorientational motion of SiH<sub>3</sub> groups. Because of this phase transition, the steep high-temperature slope of the  $R_1^H(T)$  peak cannot be described in terms of regular thermally-activated changes in  $\tau^{-1}$ ; 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  $R_1^H$ ; for example, the order-disorder transition in sodium *closo*-borate Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> near 520 K is accompanied by the two-orders-of-magnitude drop of  $R_1^H$  over the temperature interval of 5 degrees [13]. For CsSiH<sub>3</sub>, the relaxation rate drop is not so sharp; this may be related to specific features of the  $\beta - \alpha$  phase transitions in *M*SiH<sub>3</sub> 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<sub>3</sub> and RbSiH<sub>3</sub> [8]. Because of their small size (2 – 4 nm [8]), these nanodomains may be invisible in diffraction experiments. The comprehensive QENS results for CsSiH<sub>3</sub> [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<sub>3</sub> can coexist over the temperature range of at least 170 – 250 K.

The complex behavior of CsSiH<sub>3</sub> related to the order-disorder phase transition prevents us from any attempts to parameterize the  $R_1^H(T)$  data over the entire temperature range studied. Therefore, we have only tried to parameterize the  $R_1^H(T)$  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  $R_1^H(T)$  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 ~~parameterization~~[parameterization](#) of our low-temperature  $R_1^H(T)$  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

$$R_1^H = \int R_1^H(E_a)G(E_a, \bar{E}_a, \Delta E_a)dE_a \quad . \quad (2)$$

Here  $G(E_a, \bar{E}_a, \Delta E_a)$  is a Gaussian distribution function centered on  $\bar{E}_a$  with the dispersion  $\Delta E_a$ , and  $R_1^H(E_a)$  is determined by combining the standard expression that relates the relaxation rate and  $\tau$ ,

$$R_1^H(E_a) = \frac{2\Delta M_{HH}\tau}{3} \left[ \frac{1}{1 + \omega^2\tau^2} + \frac{4}{1 + 4\omega^2\tau^2} \right] , \quad (3)$$

and the Arrhenius law (Eq. (1)). The parameters of the model are the average activation energy  $\bar{E}_a$ , 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<sub>3</sub> 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  $R_1^H(T)$  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. [34](#); the corresponding fit parameters:  $\bar{E}_a = 226$  (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<sup>-2</sup>. Note that the resulting fluctuating part of the second moment,  $\Delta M_{HH}$ , corresponds to ~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<sub>3</sub> 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  $\bar{E}_a$ ). 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  $R_1^H(T)$  dependence that mimics the typical behavior for the model with a continuous jump rate distribution. Similar behavior of  $R_1^H(T)$  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*-borate salt Rb<sub>2</sub>B<sub>10</sub>H<sub>10</sub> [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<sub>3</sub> [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<sub>3</sub> 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  $\ln R_1^H$  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<sub>3</sub> above 300 K, so that the behavior of  $R_1^H$  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)  $R_1^H$  is proportional to  $\tau$ . The estimate based on an Arrhenius approximation of our  $R_1^H(T)$  data in the range 324 – 354 K gives the activation energy of 41(4) meV. This value is close to the activation energy for  $\alpha$ -phase of CsSiH<sub>3</sub> (48(2) meV) found from QENS experiments [16].

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

The evolution of the  $^{133}\text{Cs}$  NMR spectra for  $\text{CsSiH}_3$  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  $^{133}\text{Cs}$  spectra accompanied by changes in their shape. The temperature dependence of the  $^{133}\text{Cs}$  NMR line width  $\Delta_{\text{Cs}}$  (full width at half-maximum) is shown in Fig. 6. In the studied temperature range of 120 – 350 K, the most pronounced drop of  $\Delta_{\text{Cs}}$  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  $^7\text{Li}$  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  $\text{Cs}^+$  cations. For this purpose, we can use the results of the  $^{133}\text{Cs}$  spin-lattice relaxation rate measurements shown in Fig. 7.

Comparison of Figs. 7 and 4 indicates that below 300 K, the behavior of the  $^{133}\text{Cs}$  spin-lattice relaxation rate,  $R_1^{\text{Cs}}$ , resembles that of  $R_1^{\text{H}}$ . In particular, the  $R_1^{\text{Cs}}(T)$  peak is observed at nearly the same temperature as the  $R_1^{\text{H}}(T)$  peak. Thus, the observed  $^{133}\text{Cs}$  relaxation rate peak can be attributed to the reorientational motion of  $\text{SiH}_3$  groups that modulates the relatively weak  $^{133}\text{Cs} - ^1\text{H}$  dipole-dipole interaction. This is supported by the small amplitude of the  $R_1^{\text{Cs}}(T)$  peak ( $0.36 \text{ s}^{-1}$ ) which is two orders of magnitude lower than the amplitude of the  $R_1^{\text{H}}(T)$  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  $\text{SiH}_3$  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  $\text{SiH}_3$  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  $R_1^{\text{H}}$  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  $\text{Cs}^+$  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  $\sim 10^4 \text{ s}^{-1}$  (sufficient to cause the NMR line narrowing), but is still considerably lower than  $\sim 10^8 \text{ s}^{-1}$  (not reaching a new relaxation rate maximum).

## 5. Conclusions

The results of our proton NMR measurements indicate that  $[\text{SiH}_3]^-$  groups in  $\text{CsSiH}_3$  retain unusually high reorientational mobility down to low temperatures. According to the  $^1\text{H}$  NMR line width measurements, even at  $T = 14 \text{ K}$  the jump rate of  $\text{SiH}_3$  reorientations in  $\text{CsSiH}_3$  is about  $10^5 \text{ s}^{-1}$ . In agreement with recent QENS results for  $\text{CsSiH}_3$  [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  $\text{SiH}_3$  reorientations leads to the considerable drop of the measured  $^1\text{H}$  spin-lattice relaxation rate  $R_1^H$ ; however, this drop is not as abrupt as in the case of the order-disorder transitions in borohydrides [34] and *closo*-borates [13]. The smearing of the  $R_1^H$  “step” in the phase transition region for  $\text{CsSiH}_3$  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  $\text{CsSiH}_3$ , the activation energy for  $\text{SiH}_3$  reorientations estimated from our  $R_1^H(T)$  data is 41(4) meV. The  $^{133}\text{Cs}$  NMR results are consistent with the onset of diffusive motion of  $\text{Cs}^+$  ions at the frequency scale of  $\sim 10^4 \text{ s}^{-1}$  above 300 K.

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## Figure captions

**Fig. 1.** Evolution of the proton NMR spectrum for CsSiH<sub>3</sub> with temperature.

**Fig. 2.** Temperature dependence of the width (full width at half-maximum) of the <sup>1</sup>H NMR spectrum measured for CsSiH<sub>3</sub> at 28 MHz.

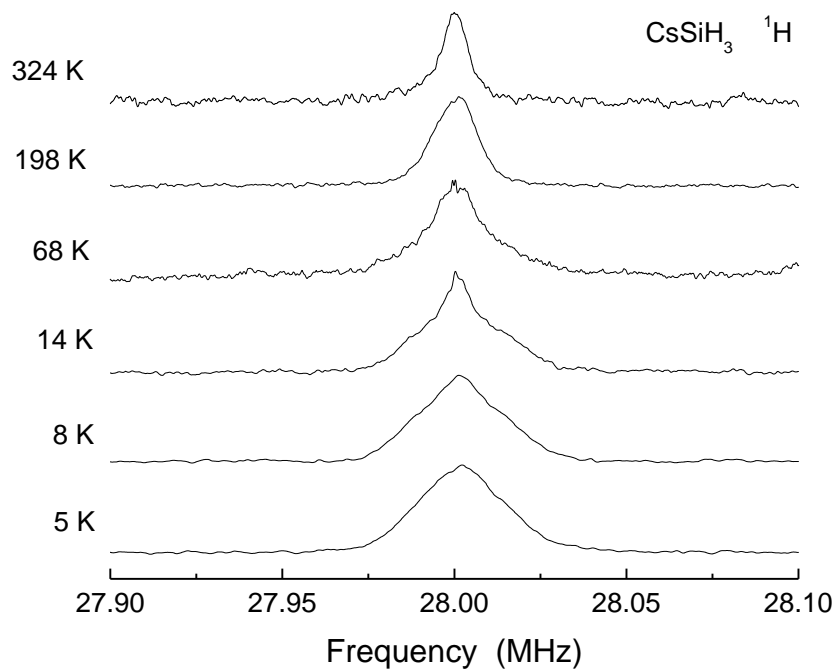
**Fig. 3.** Schematic view of the structure of β-CsSiH<sub>3</sub> (along the *c* axis). Olive spheres: Cs atoms; gray spheres: Si atoms; blue spheres: H atoms.

**Fig. 4.** Proton spin-lattice relaxation rates measured at 28 and 90 MHz for CsSiH<sub>3</sub> 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 – 200 K.

**Fig. 5.** Evolution of the <sup>133</sup>Cs NMR spectrum for CsSiH<sub>3</sub> with temperature.

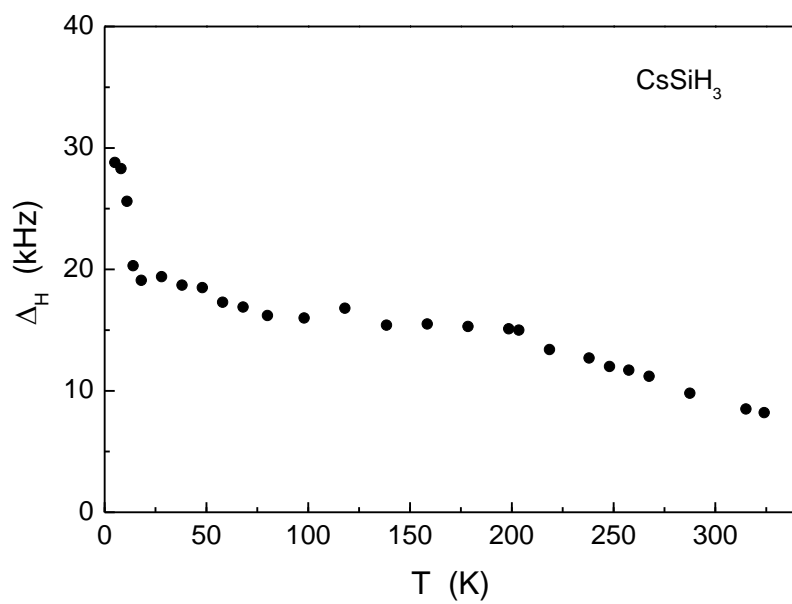
**Fig. 6.** Temperature dependence of the width (full width at half-maximum) of the <sup>133</sup>Cs NMR spectrum measured for CsSiH<sub>3</sub> at 65.62 MHz.

**Fig. 7.** <sup>133</sup>Cs spin-lattice relaxation rate measured at 65.62 MHz for CsSiH<sub>3</sub> as a function of the inverse temperature.

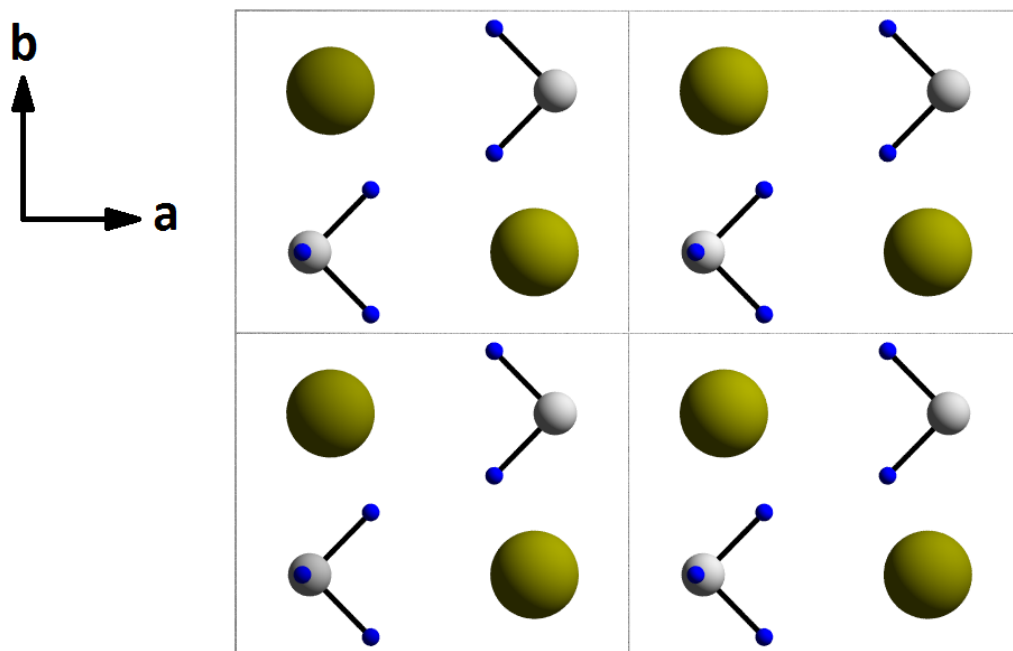


**Fig. 1.** Evolution of the proton NMR spectrum for  $\text{CsSiH}_3$  with temperature.

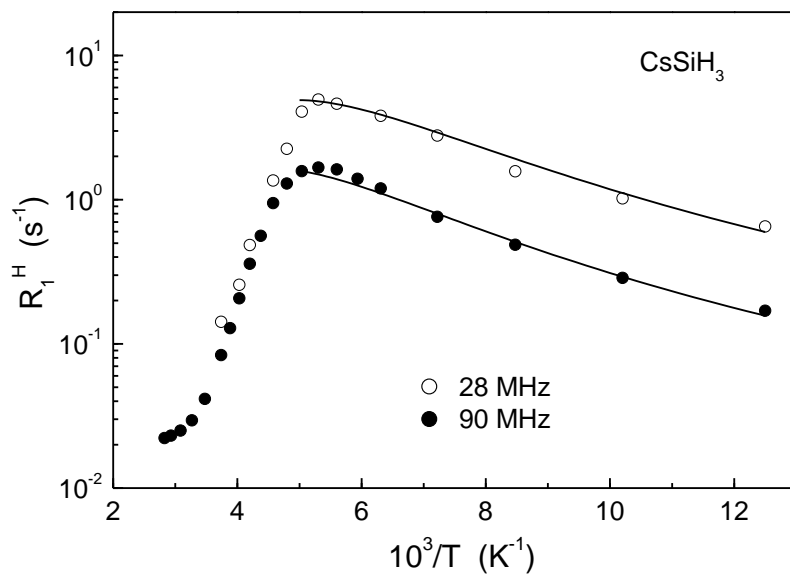




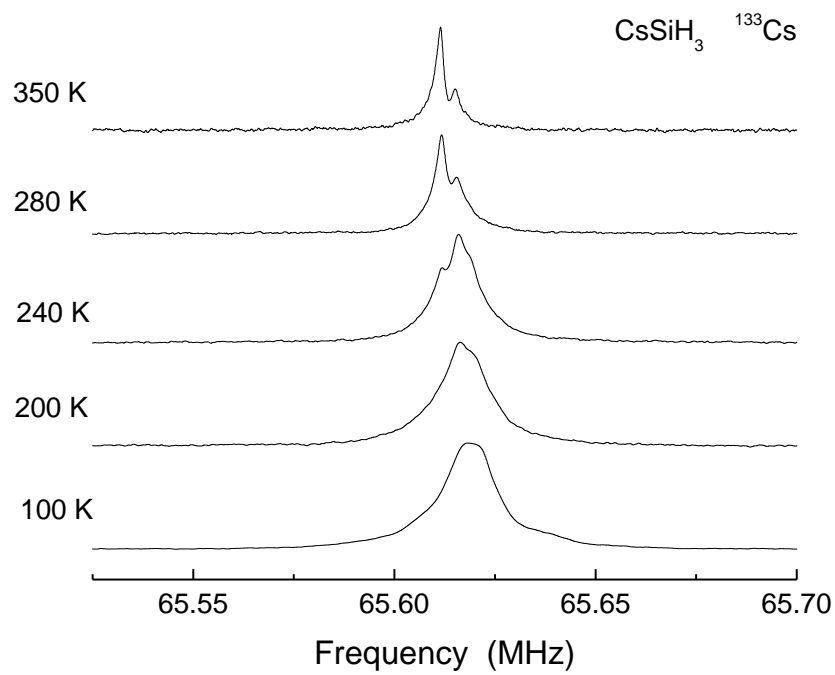
**Fig. 2.** Temperature dependence of the width (full width at half-maximum) of the  $^1\text{H}$  NMR spectrum measured for  $\text{CsSiH}_3$  at 28 MHz.



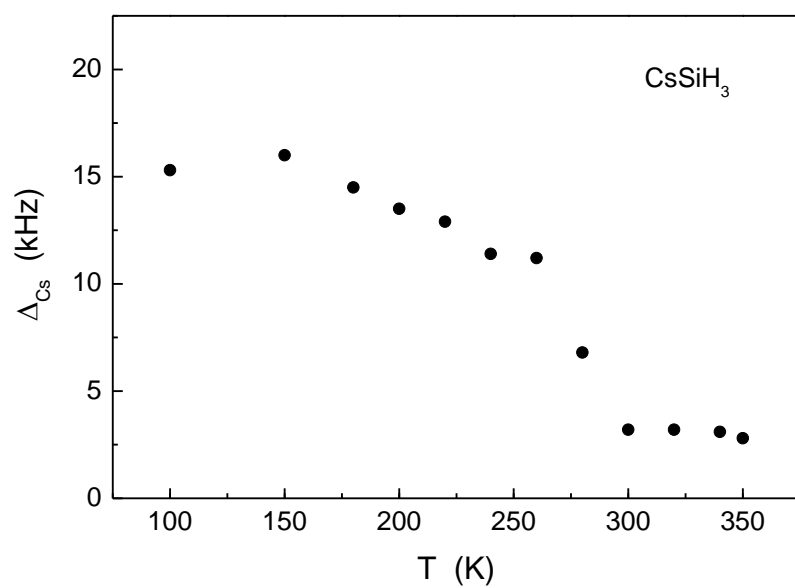
**Fig. 3.** Schematic view of the structure of  $\beta$ -CsSiH<sub>3</sub> (along the  $c$  axis). Olive spheres: Cs atoms; gray spheres: Si atoms; blue spheres: H atoms.



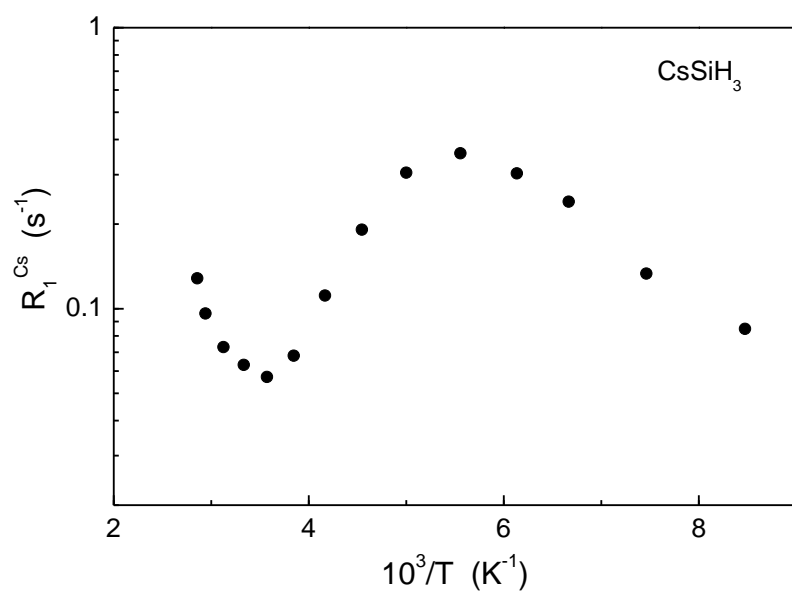
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**Fig. 7.**  $^{133}\text{Cs}$  spin-lattice relaxation rate measured at 65.62 MHz for  $\text{CsSiH}_3$  as a function of the inverse temperature.