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# Tracking the Progression of Anion Reorientational Behavior between $\alpha$ -Phase and $\beta$ -Phase Alkali-Metal Silanides, MSiH<sub>3</sub>, by **Quasielastic Neutron Scattering**

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Supporting Information

ABSTRACT: Quasielastic neutron scattering (QENS) measurements over a wide range of energy resolutions were used to probe the reorientational behavior of the pyramidal  $SiH_3^-$  anions in the monoalkali silanides (MSiH<sub>3</sub>) where M = K, Rb, and Cs) within the low-temperature ordered  $\beta$ -phases, and for CsSiH<sub>3</sub>, the high-temperature disordered  $\alpha$ -phase and intervening hysteretic transition region. Maximum jump frequencies of the  $\beta$ -phase anions near the  $\beta - \alpha$  transitions range from around 10<sup>9</sup> s<sup>-1</sup> for  $\beta$ -KSiH<sub>3</sub> to 10<sup>10</sup> s<sup>-1</sup> and higher for  $\beta$ -RbSiH<sub>3</sub> and  $\beta$ -CsSiH<sub>3</sub>. The  $\beta$ -phase anions undergo uniaxial 3-fold rotational jumps around the anion quasi- $C_3$  symmetry axis. CsSiH<sub>3</sub> was the focus of further studies to map out the evolving anion dynamical behavior at temperatures above the  $\beta$ -phase region. As in  $\alpha$ -KSiH<sub>3</sub> and  $\alpha$ -RbSiH<sub>3</sub>, the highly mobile anions (with reorientational jump frequencies approaching and exceeding  $10^{12}$  s<sup>-1</sup>) in the disordered  $\alpha$ -CsSiH<sub>3</sub> are all adequately modeled



by H jumps between 24 different locations distributed radially around the anion center of gravity, although even higher anion reorientational disorder cannot be ruled out. QENS data for CsSiH<sub>3</sub> in the transition region between the  $\alpha$ - and  $\beta$ -phases corroborated the presence of dynamically distinct intermediate (i-) phase. The SiH<sub>3</sub><sup>-</sup> anions within *i*-phase appear to undergo uniaxial small-angular-jump reorientations that are more akin to the lower-dimensional  $\beta$ -phase anion motions rather than to the multidimensional  $\alpha$ -phase anion motions. Moreover, they possess orientational mobilities that are an order-of-magnitude lower than those for  $\alpha$ -phase anions but also an order-of-magnitude higher than those for  $\beta$ -phase anions. Combined QENS and neutron powder diffraction results strongly suggest that this i-phase is associated chiefly with the more short-range-ordered, nanocrystalline portions (invisible to diffraction) that appear to dominate the CsSiH<sub>3</sub>.

# INTRODUCTION

Alkali-metal silanides ( $MSiH_3$ , M = K, Rb, and Cs) have recently gained attention as potential hydrogen-storage compounds due to their reversible dehydrogenation/hydrogenation properties.<sup>1-5</sup> Typically, a silanide↔silicide equilibrium (i.e.,  $MSiH_3 \leftrightarrow MSi + 1.5H_2$ ) exists, providing favorable hydrogen vapor pressures of 0.1 MPa near 410 K.<sup>3</sup> All MSiH<sub>3</sub> compounds studied, including the various alkali-metal-alloy versions  $(K_{0.5}Cs_{0.5}SiH_3, K_{0.5}Rb_{0.5}SiH_3, and Rb_{0.5}Cs_{0.5}SiH_3)$ undergo hysteretic phase transitions upon heating and cooling between ordered monoclinic or orthorhombic  $\beta$ -phase structures to disordered face-centered-cubic  $\alpha$ -phase structures<sup>3,6–9</sup> (see Figure 1). In contrast to the crystallographically

ordered,  $\beta$ -phase SiH<sub>3</sub><sup>-</sup> anions, the  $\alpha$ -phase anions exhibit three-dimensional orientational disorder. Neutron scattering fixed-window-scans (FWSs)9 and differential scanning calorimetry/heat capacity measurements<sup>3,10</sup> in heating and cooling regimens confirm that the transitions between  $\alpha$ -MSiH<sub>3</sub> and  $\beta$ -MSiH<sub>3</sub> phases are highly hysteretic.

An NMR wide-line investigation,<sup>7</sup> as well as neutron total scattering and infrared, Raman, and neutron vibrational spectroscopy measurements in conjunction with density functional theory calculations<sup>11,12</sup> suggested that this  $\alpha$ -phase

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Figure 1. Structural differences between the ordered  $\beta$ -MSiH<sub>3</sub> and disordered  $\alpha$ -MSiH<sub>3</sub> (M = K, Rb, Cs) phases showing the respective near-neighbor cation environments (7-coordination for the former and 6-coordination for the latter). M<sup>+</sup> alkali metal cations are denoted by green spheres, whereas the pyramidal SiH<sub>3</sub><sup>-</sup> anions are denoted by blue Si spheres and white H spheres. Although one specific anion orientation is highlighted in  $\alpha$ -MSiH<sub>3</sub>, the multiple H atoms distributed radially around the Si atom represent all of the possible H positions associated with the orientationally disordered SiH<sub>3</sub><sup>-</sup> anions in this structure. N.B., *i*-MSiH<sub>3</sub> is meant to be a general term to denote the possible formation of "intermediate" phases in the transition regions with intermediate SiH<sub>3</sub><sup>-</sup> anion orientational mobilities between those for the  $\beta$ -MSiH<sub>3</sub> and  $\alpha$ -MSiH<sub>3</sub> phases.

anion disorder was dynamical in nature. Subsequent quasielastic neutron scattering (QENS) measurements of the  $\hat{\alpha}$ -MSiH<sub>3</sub> phases<sup>9,13</sup> confirmed rapid reorientational mobilities  $(>10^{12} \text{ small-angular jumps s}^{-1})$  for the orientationally disordered SiH<sub>3</sub><sup>-</sup> anions above room temperature. The momentum-transfer dependence of the quasielastic scattering was typically consistent with a three-dimensional reorientational jump mechanism in which the three H atoms of each rigid-body SiH<sub>3</sub><sup>-</sup> anion traverse the surface of a sphere that is roughly centered on the Si atom. The QENS data were more in accordance with reorientational jumps between multiple yet discrete H positions (being successfully modeled as jumps among the 24 different, neutron-powder-diffraction-derived, crystallographic H positions previously used to describe the orientational disorder<sup>3</sup>) rather than fully isotropic (random walk) rotational diffusion.

Additional FWS measurements for all monoalkali and dialkali-metal silanides have indicated orders-of-magnitude lower anion orientational mobilities in the ordered  $\beta$ -phases,<sup>9</sup> a finding in general agreement with subsequent Raman, heat capacity, and <sup>2</sup>H NMR investigations of KSi(H/D)<sub>3</sub> and RbSi(H/D)<sub>3</sub>.<sup>10</sup> Interestingly, these and other QENS data showed that the anion mobility in the  $\beta$ -phase monoalkali silanides trended higher with increasing alkali-metal-cation size, whereas the opposite trend was observed in the  $\alpha$ -phases.<sup>9,13</sup> Moreover, in contrast to the highly disordered  $\alpha$ -phases, the single crystallographic orientations for each SiH<sub>3</sub><sup>--</sup> anion in the ordered  $\beta$ -phases point to only one physically reasonable  $\beta$ -phase reorientational mechanism, i.e., uniaxial 3-fold rotational jumps of the H atoms around the anion's nominal  $C_3$  symmetry axis.

A recent study by Nedumkandathil et al.<sup>10</sup> focusing on the order–disorder rotator-phase transition in KSiH<sub>3</sub> and RbSiH<sub>3</sub> used <sup>2</sup>H NMR to show that presumably nanosized (2–4 nm) disordered  $\alpha$ -like domains persisted well below the  $\alpha$ -phase to  $\beta$ -phase transition temperature delineated by heat capacity measurements upon cooling. Moreover, QENS data suggested that these  $\alpha$ -like nanodomains possess a markedly reduced

SiH<sub>3</sub><sup>-</sup> anion orientational mobility, with significantly longer relaxation times on the order of picoseconds instead of the 0.2–0.3 ps between reorientational jumps observed for bulk  $\alpha$ -phase above the phase transition. It was surmised that a rather weak coordination of SiH<sub>3</sub><sup>-</sup> anions among the alkali metal cations was the cause of such lingering disordered subcooled nanophases.

In the current paper, high-resolution QENS measurements are used to fully characterize the alkali-metal-dependent anion reorientational dynamics in three  $\beta$ -MSiH<sub>3</sub> compounds (M = K, Rb, and Cs) as well as the unusual nature of the rotatorphase transition between the  $\beta$ -phases and  $\alpha$ -phases for CsSiH<sub>3</sub>. These QENS results bolster the general conclusion of the previous NMR/QENS study<sup>10</sup> that distinct subcooled intermediate phases exist and exhibit anion orientational mobilities intermediate between those for the  $\alpha$ -phases and  $\beta$ -phases. The suggested nature of the SiH<sub>3</sub><sup>-</sup> anion reorientations in the intermediate CsSiH<sub>3</sub> phase also points to an *intermediate mechanistic* behavior to those for the  $\alpha$ -phase and  $\beta$ -phase. Complementary temperature-dependent neutron powder diffraction (NPD) measurements for CsSiD<sub>3</sub> lead us to conclude that this intermediate phase is associated with the significant fraction of nanosized crystallites presumably present in the material.

# **EXPERIMENTAL DETAILS**

MSi (M = K, Rb, and Cs) alloys of the order of 1 g each were synthesized by high-temperature annealing of 1:1.03 atomic ratios of metal to silicon, using potassium (99.95%, Sigma-Aldrich,<sup>14</sup> rubidium (99.75%, Alfa Aesar), cesium (99.8%, Alfa Aesar), and silicon (powder, - 325 mesh Sigma-Aldrich) starting materials. All materials were handled in an argon-filled glovebox. Each mixture was arc-weld-sealed within a stainlesssteel ampule inside the glovebox. The ampules were typically heated 1 K min<sup>-1</sup> from room temperature to 773 K for KSi, and to 873 K for all other alloys, holding them for 48 h before cooling 0.2 K min<sup>-1</sup> back down to room temperature. A slight excess of silicon was added to ensure that all the starting alkali metals were reacted. All resulting MSi samples were first activated via evacuation at 473 K for 12 h and then hydrogenated at 373 K with ca. 5 MPa of hydrogen for up to 24 h. An additional, deuterated CsSiD<sub>2</sub> sample for NPD measurements was synthesized in the same fashion and was the same material used in ref 3.

Quasielastic neutron scattering measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) on the Disk Chopper Spectrometer (DCS),<sup>15</sup> High-Flux Backscattering Spectrometer (HFBS),<sup>16</sup> and NGA Neutron Spin-Echo spectrometer (NSE).<sup>17</sup> DCS measurements utilized incident neutron wavelengths of 2.75 Å (10.8 meV), 4.8 Å (3.55 meV), 6 Å (2.27 meV), and 8 Å (1.28 meV) with respective resolutions of 275, 56, 30, and 30 µeV full width at halfmaximum (fwhm) and respective maximum attainable Q values of around 4.30, 2.46, 1.98, and 1.48 Å<sup>-1</sup>. The instrumental resolution function was determined from the measured QENS spectrum at 25 K in all cases. The measurements were performed on CsSiH<sub>3</sub> at multiple temperatures in the range from 170 to 350 K, in both heating and cooling regimens. Additional corroborating measurements were performed on RbSiH<sub>3</sub> at 281 K after cooling from 300 K. HFBS measurements utilized an incident neutron wavelength of 6.27 Å, yielding a resolution of 0.8  $\mu$ eV fwhm. QENS

measurements on the HFBS spectrometer were performed on  $CsSiH_3$ ,  $RbSiH_3$ , and  $KSiH_3$  in the temperature range from 150 to 300 K. The instrumental resolution function was determined from the measured QENS spectrum at 4 K. NSE measurements were performed on  $CsSiH_3$  at 140 K (and at 4 K for the resolution) utilizing an incident neutron wavelength of 6.0 Å at (2.27 meV,  $\Delta\lambda/\lambda \approx 0.18$ ) for Fourier times up to 17.5 ns at Q = 0.8 Å<sup>-1</sup>. NPD measurements on  $CsSiD_3$  were performed at the Institut Laue Langevin (ILL, Grenoble, France) on the D1B diffractometer ( $\lambda = 1.289$  Å).

Data were analyzed using Mslice and PAN programs within the DAVE software package.<sup>18</sup> Standard uncertainties in all figures in the text and Supporting Information, if not explicitly indicated, are commensurate with the observed scatter in the data.

### RESULTS AND DISCUSSION

**MSiH<sub>3</sub>**  $\beta$ -Phase Dynamics. Figure S1 in the Supporting Information illustrates neutron FWS data for MSiH<sub>3</sub> (M = K, Rb, and Cs), adapted from ref 9, upon both heating and cooling regimens, which reveals the significant hystereses in SiH<sub>3</sub><sup>-</sup> orientational mobilities reflecting the hysteretic phase change behaviors for these compounds. Thus, it is important to emphasize that the relative fractions of compound phases present at any particular temperature depends strongly on the temperature history. Since the FWSs indicate considerably low SiH<sub>3</sub><sup>-</sup> orientational mobilities for the various  $\beta$ -MSiH<sub>3</sub> phases, these particular mobilities could only be practically probed using the two highest-resolution spectrometers, namely HFBS and NSE, during heating regimens from low to high temperatures which ensure higher hysteretic  $\beta-\alpha$  phase boundary temperatures.

Representative QENS spectra of  $\beta$ -KSiH<sub>3</sub>,  $\beta$ -RbSiH<sub>3</sub>, and  $\beta$ -CsSiH<sub>3</sub> at Q values of 1.16  $Å^{-1}$  obtained on the HFBS spectrometer and measured at temperatures of 292, 260, and 200 K, respectively, are shown in Figure 2. In all cases, the spectra were fit with a delta function (elastic scattering) and one Lorentzian function, both convoluted with the instrumental resolution function, above a flat background. Indeed, the constant O-dependences of the quasielastic line widths obtained for all compounds (Figure 3) are consistent with the three-site jump model,<sup>19</sup> which is expected for the  $\beta$ -phase and in which H atoms are reorienting by 120° jumps about the nominal 3-fold symmetry axis of the SiH<sub>3</sub><sup>-</sup> group. Again, we stress that such a model is dictated by the ordered crystallographic structures of the  $\beta$ -phases, which restricts the possible H positions to three locations around the directionally invariant, anion  $C_3$  axis.

Figure 4 illustrates the temperature-dependent linewidths for the  $\beta$ -phase compounds plotted in an Arrhenius fashion. The fundamental jump correlation frequencies  $\tau_1^{-1}$  are calculated from the Lorentzian fwhm linewidths  $\Gamma$  by  $\tau_1^{-1} = \Gamma/(2\hbar)$ . The slope of  $\ln(\tau_1^{-1})$  vs  $T^{-1}$  is  $-E_a/k_B$ , where  $E_a$  is the activation energy for anion reorientation and  $k_B$  is the Boltzmann constant. For  $\beta$ -CsSiH<sub>3</sub>, QENS measurements were extended further down in temperature to 140 K using the NSE spectrometer (see Figure S2 for data and analysis). Table 1 lists fitted  $E_a$  values of 160(2), 190(2), and 105(2) meV for  $\beta$ -KSiH<sub>3</sub>,  $\beta$ -RbSiH<sub>3</sub>, and  $\beta$ -CsSiH<sub>3</sub>, respectively. At first glance, there appears to be no monotonic trend between  $E_a$  and unit cell size, contrary to what one might expect based on previous reports of similar local 7-fold alkali-metal-cation coordination environments surrounding each  $\beta$ -phase SiH<sub>3</sub><sup>-</sup> anion. One



**Figure 2.** Exemplary QENS spectra of (a)  $\beta$ -KSiH<sub>3</sub>, (b)  $\beta$ -RbSiH<sub>3</sub>, and (c)  $\beta$ -CsSiH<sub>3</sub> at Q values of 1.16 Å<sup>-1</sup> obtained on the HFBS spectrometer and measured at temperatures of 292, 260, and 200 K, respectively. Spectra were fit with a delta function and one Lorentzian component, both convoluted with the instrumental resolution function, on top of a flat background.



Figure 3. Q-dependence of the Lorentzian (quasielastic) fwhm line widths for  $\beta$ -KSiH<sub>3</sub>,  $\beta$ -RbSiH<sub>3</sub>, and  $\beta$ -CsSiH<sub>3</sub> obtained on the HFBS spectrometer and measured at temperatures of 292, 260, and 200 K, respectively.

caveat is that, due to the specific details of  $\beta$ -KSiH<sub>3</sub> phase behavior and particularly low associated anion mobility, we are only able to assess a rather limited 20 K temperature range (280 to 300 K) for this compound. This leads to more uncertainty in the fitted  $E_a$  value. In fact, solid-state <sup>2</sup>H NMR spectroscopic results for  $\beta$ -KSiD<sub>3</sub><sup>10</sup> suggest to us anion reorientational jump frequencies of roughly the order of 10<sup>5</sup> s<sup>-1</sup> by 200 K based on the temperature dependence of the <sup>2</sup>H NMR spectra. Inclusion of this extra data point in our analysis (see Figure 4) would lead to a much higher fitted  $E_{a}$  value of 517(3) meV. Yet, we note that the 200 K jump frequency for the lighter H-isotope  $\beta$ -KSiH<sub>3</sub> is likely somewhat higher due to the higher expected torsional attempt frequency (e.g., by a factor of  $\sqrt{2}$  in the harmonic case) for H vs D. Nonetheless, even if we assume a 10-fold-larger  $\tau_1^{-1}$  value at 200 K for  $\beta$ -KSiH<sub>3</sub>, this would still yield a larger  $E_{a}$  value [383(3) meV] than for  $\beta$ -RbSiH<sub>3</sub>. Hence it is not unreasonable to assume that a trend does actually exist between  $E_{1}$  and unit cell size, with both lower anion mobilities and higher activation energy barriers resulting in general from smaller, more sterically restrictive anion sites. In contrast to the comparatively similar anion mobilities reported for all three different  $\alpha$ -phase compounds,<sup>9,13</sup> the trending differences in anion mobilities between  $\beta$ -phase compounds are particularly dramatic, as exemplified in Figure 4 by the two-orders-of-magnitude less mobile anions in  $\beta$ -KSiH<sub>3</sub> compared to those in  $\beta$ -CsSiH<sub>3</sub> extrapolated to the same temperatures.

While we make this comparison, it is worth mentioning that the most recent neutron powder diffraction patterns<sup>10</sup> following the structural evolution of  $\beta$ -KSiD<sub>3</sub> and  $\beta$ -RbSiD<sub>3</sub> with increasing temperature suggested that the latter compound begins distorting slightly from its original lowtemperature monoclinic structure with increasing temperature starting somewhere above 200 to 210 K. By 240 K a triclinically distorted  $\beta$ -RbSiD<sub>3</sub> structure appeared to provide a better fit to the data before further transformation to the  $\alpha$ phase at higher temperature. This proposed triclinic transformation was bolstered by complementary NMR, Raman, and heat capacity measurements.<sup>10</sup> In contrast,  $\beta$ -KSiD<sub>3</sub> did not



Article



400

300 250

 $\alpha$ -RbSiH<sub>3</sub>

**Figure 4.** Anion jump correlation frequencies  $\tau_1^{-1}$  vs 1/T for various KSiH<sub>3</sub>, RbSiH<sub>3</sub>, and CsSiH<sub>3</sub> phases plotted in an Arrhenius fashion as determined from measurements on DCS, HFBS, and NSE spectrometers. DCS measurements were performed with neutron wavelengths of 2.75 (circles), 4.8 (diamonds), 6 (triangles), and 8 Å (pentagons) with respective fwhm resolutions of 275, 56, 30, and 30  $\mu$ eV. HFBS measurements are presented by squares, obtained with 6.27 Å wavelength neutrons with a fwhm resolution of 0.8  $\mu$ eV. The NSE measurement (star) was obtained with 6.0 Å wavelength neutrons. Filled and open symbols indicate measurements during cooling and heating regimens, respectively. The dashed line for  $\beta$ -KSiH<sub>3</sub> represents the linear fit obtained upon inclusion of an anion reorientational jump frequency of 10<sup>5</sup> s<sup>-1</sup> at 200 K estimated from prior NMR measurements.<sup>10</sup>

Table 1. Comparison of Activation Energies for **Reorientations Determined from QENS Data** 

compound	QENS activation energy (meV)	compound	QENS activation energy (meV)
$\alpha$ -KSiH <sub>3</sub>	$39(1)^{13}$	$\beta$ -KSiH <sub>3</sub>	160(2)
			517(3) <sup>a</sup>
$\alpha$ -RbSiH <sub>3</sub>	$33(1)^{13}$	$\beta$ -RbSiH <sub>3</sub>	190(2)
$\alpha$ -CsSiH <sub>3</sub>	48(2)	$\beta$ -CsSiH <sub>3</sub>	105(2)
	$32(3)^9$		

 $^a$ This fitted value is based on an additional assumed  $au_1^{-1}$  value of 10 $^5$ s<sup>-1</sup> at 200 K estimated from NMR data from ref10.

seem to deviate from its low-temperature orthorhombic structure, and there was no further comparative study undertaken for  $\beta$ -CsSiD<sub>3</sub>. On the basis of this information, we cannot rule out that a progressive triclinic distortion with increasing temperature, although minor, is noticeably affecting the corresponding SiH<sub>3</sub><sup>-</sup> mobilities and reorientational barriers determined from the  $\beta$ -RbSiH<sub>3</sub> QENS results (and possibly even the  $\beta$ -CsSiH<sub>3</sub> results).

There is general agreement between the  $\beta$ -phase results in Figure 4 and the FWSs in Figure S1. Anion reorientational



**Figure 5.** Exemplary QENS spectra for CsSiH<sub>3</sub> (in cooling) at 270 K ((a)  $Q = 1.20 \text{ Å}^{-1}$  and (b)  $Q = 2.20 \text{ Å}^{-1}$ ) and 240 K ((c)  $Q = 1.20 \text{ Å}^{-1}$  and (d)  $Q = 2.20 \text{ Å}^{-1}$ ) using 4.8 Å wavelength neutrons (with 56  $\mu$ eV fwhm resolution). Spectra were fit with a delta function and three Lorentzian components, all four convoluted with the instrumental resolution function, on top of a flat background.

jump frequencies reach about  $10^8 \text{ s}^{-1}$  by around 250, 175, and 125 K for  $\beta$ -KSiH<sub>3</sub>,  $\beta$ -RbSiH<sub>3</sub>, and  $\beta$ -CsSiH<sub>3</sub>, respectively. (N.B., we previously quoted somewhat lower respective temperatures of ~225, 150, and 80 K based on the observed earliest onset of accelerating FWS intensity loss,<sup>9</sup> but it is clear now that these estimated threshold points more accurately reflected slightly smaller  $\tau_1^{-1}$  values somewhere between  $10^7$ and  $10^8 \text{ s}^{-1}$ .) At the higher temperatures, in contrast with  $\beta$ -KSiH<sub>3</sub>, which never attains reorientational jump frequencies above  $\approx 10^9$  s<sup>-1</sup> before transformation to the  $\alpha$ -phase,  $\beta$ -RbSiH<sub>3</sub> and  $\beta$ -CsSiH<sub>3</sub> respectively reach and exceed 10<sup>10</sup> s<sup>-1</sup> by the time they undergo their  $\beta - \alpha$  transformations. Therefore, the FWS intensities for the latter two clearly begin plateauing out (which reflects the quasielastic component widths becoming too overly broad and disappearing into the flat HFBS baseline scattering) during heating regimens on approach to their  $\alpha$ -phases, whereas the corresponding FWS intensity for  $\beta$ -KSiH<sub>3</sub> continues dropping within the  $10^8 - 10^{10}$  s<sup>-1</sup> frequency window of the spectrometer until it suddenly and more steeply collapses further toward its lower  $\alpha$ -phase plateau, like the other two congeners. This universal drop to a lower  $\alpha$ -phase plateau simply reflects an increase in the expected fraction of quasielastic scattering due to the transition in SiH<sub>3</sub><sup>-</sup> reorientational mechanism from  $\beta$ phase uniaxial reorientations to  $\alpha$ -phase three-dimensional sphere-tracing reorientations.

**CsSiH<sub>3</sub>**  $\alpha$ -Phase and Transition-Region Dynamics. In comparison to the  $\beta$ -phases, the  $\alpha$ -phases exhibit orders-of-magnitude-higher anion orientational mobilities. From an experimental viewpoint, it is apparent that  $\alpha$ -CsSiH<sub>3</sub> is the best of the three  $\alpha$ -phase silanides to investigate because it provides the widest temperature range accessible within the neutron scattering resolution windows of our instruments. Thus, to gain more insights into SiH<sub>3</sub><sup>-</sup> dynamics in the  $\alpha$ -phases and the nature of the rotator-phase transition, we focused our attention on  $\alpha$ -CsSiH<sub>3</sub> and  $\beta$ -CsSiH<sub>3</sub>.

Figure 5 illustrates T-dependent QENS spectra of  $\alpha$ -CsSiH<sub>2</sub> measured on the DCS spectrometer at Q values of 1.20 and 2.20  $Å^{-1}$  and temperatures of 270 and 240 K attained upon cooling from 350 K. In line with prior results for  $\alpha$ -KSiH<sub>3</sub>,  $\alpha$ -RbSiH<sub>3</sub>, and  $\alpha$ -CsSiH<sub>3</sub>,<sup>9,10,13</sup> the QENS spectra were initially fit with a resolution-convoluted line shape comprised of one elastic component (delta function) together with two Lorentzian functions. However, the higher-resolution measurements with wavelengths of 4.8 and 6 Å clearly indicated the need for inclusion of an additional narrower Lorentzian component. Thus, a reasonable spectral fit required three Lorentzian components with order-of-magnitude-different widths, in addition to an elastic peak component and a flat background. The two narrower Lorentzian components are associated with quasielastic scattering from SiH<sub>3</sub><sup>-</sup> anion reorientations, while the very broad Lorentzian is consistent with low-energy inelastic scattering from overdamped anion vibrational modes, as observed previously for QENS measurements of  $\alpha$ -KSiH<sub>3</sub>,  $\alpha$ -RbSiH<sub>3</sub>, and  $\alpha$ -CsSiH<sub>3</sub>,  ${}^{9,10,13}$  as well as for other systems with highly mobile anions such as the disordered Li and Na decahydro-closo-deca(carba)borate salts.<sup>20</sup> This is further confirmed by the  $Q^2 \exp(-Q^2 \langle u^2 \rangle)$ dependence of the intensity, where  $\langle u^2 \rangle$  is the mean-squared displacement and  $\exp(-Q^2\langle u^2\rangle)$  is the Debye–Waller factor, which is in line with the expected behavior for the scattering intensity of an overdamped vibrational feature (see Figure S3). The fitted root-mean-squared H displacement for this feature was 0.38(3) Å, which one can interpret as the rough oscillatory distance transversed by the H atoms within localized wells comprising the corrugated rotational potential landscape, distinct from the longer-distance, much-lower-frequency H rotational jumps between these wells leading to the quasielastic scattering components.

Figure 6 presents the Q-dependences of the quasielastic linewidths of the two narrower Lorentzian components of  $\alpha$ -



**Figure 6.** Q-dependence of the two narrower Lorentzian (quasielastic) fwhm linewidths  $\Gamma$  for CsSiH<sub>3</sub> (in cooling) at 270 K measured with 4.8 (red symbols) and 6.0 Å (dark red symbols) wavelength neutrons with respective fwhm resolutions of 56 and 30  $\mu$ eV.

CsSiH<sub>3</sub> measured at 270 K. The increasing line width of the broader component with Q above about 1.5 Å<sup>-1</sup> indicates similar behavior to what was previously observed for  $\alpha$ -KSiH<sub>3</sub> and  $\alpha$ -RbSiH<sub>3</sub>,<sup>13</sup> and signals a small-angle jump-diffusion mechanism with fundamental jump correlation frequencies  $\tau_1^{-1}$  of the order of 10<sup>11</sup> to 10<sup>12</sup> s<sup>-1</sup>, which is in the expected range of anion mobilities in the  $\alpha$ -phase.

Although the second Lorentzian component is almost an order of magnitude narrower than the broader bulk  $\alpha$ -phase component discussed above, it is still almost an order of magnitude broader than the quasielastic component found earlier for the  $\beta$ -CsSiH<sub>3</sub> phase, so it presumably marks the presence of a third dynamically distinctive phase. The relatively constant line width with increasing Q for this component in Figure 6 compared to that for the  $\alpha$ -phase suggests an anion reorientational mechanism more in accord with a uniaxial H jump mechanism as for  $\beta$ -phase SiH<sub>3</sub><sup>-</sup> anions, but of much higher mobility. For lack of a better term, we refer to this coexisting "intermediate" phase as the *i*-phase.

Figure 4 includes the Arrhenius-type plots for  $\tau_1^{-1}$  (and corresponding linewidths) for the  $\alpha$ - and *i*-phases of CsSiH<sub>3</sub> during both heating and cooling regimens. For the  $\alpha$ -phases, the average linewidths were calculated for Q values <1.5 Å<sup>-1</sup> (the flat region in Figure 6). For the *i*-phases (as for the  $\beta$ -phases), the averaging of linewidths included all Q values.

The  $\tau_1^{-1}$  data indicate SiH<sub>3</sub><sup>-</sup> anion reorientational jump frequencies for disordered  $\alpha$ -CsSiH<sub>3</sub> between around 3 × 10<sup> $\overline{11}$ </sup>  $s^{-1}$  and 2  $\times$  10<sup>12</sup>  $s^{-1}$ , in accordance with the prior QENS results.<sup>9,10,13</sup> This is in contrast to the much less mobile anions in the ordered  $\beta$ -phases for all compounds, almost 2 orders of magnitude slower in comparison to the  $\alpha$ -phase, leaving them in the range from  $2 \times 10^{8}$  s<sup>-1</sup> to  $1 \times 10^{10}$  s<sup>-1</sup>. The much lower anion mobility in the ordered  $\beta$ -phases compared to the disordered  $\alpha$ -phases is expected, due to the smaller (more sterically restrictive) unit cell volume for the former. The  $\tau_1^{-1}$ values for *i*-CsSiH<sub>3</sub> are clearly intermediate between those for the  $\alpha$ - and  $\beta$ -phases, ranging from around  $2 \times 10^{10}$  to  $3 \times 10^{11}$ s<sup>-1</sup>. The temperature dependences of the *i*-CsSiH<sub>3</sub> and  $\alpha$ -CsSiH<sub>3</sub>  $\tau_1^{-1}$  values in Figure 4 are found to be largely unaffected by thermal history, even if their relative phase fractions (as determined by the QENS data) may differ somewhat between heating and cooling regimens. This varies somewhat from the behavior that was previously reported for the "undercooled  $\alpha$ -phases" for KSiH<sub>3</sub> and RbSiH<sub>3</sub><sup>10</sup> where there were order-of-magnitude differences in effective  $\tau_1^{-1}$ values depending on whether these phases were "remnant" (i.e., remaining upon cooling down from the  $\alpha$ -phases) or "premonitory" (i.e., appearing upon heating up from the  $\beta$ phases). Hence, it is possible that the details of the structural and dynamical evolution in the transition region for CsSiH<sub>3</sub> are somewhat different than those seen for KSiH<sub>3</sub> and RbSiH<sub>3</sub>.

The simplest picture in agreement with our CsSiH<sub>3</sub> results points to the temperature-dependent formation of three dynamically distinct phases ( $\beta$ -CsSiH<sub>3</sub>, *i*-CsSiH<sub>3</sub>, and  $\alpha$ -CsSiH<sub>3</sub>). Unlike for KSiH<sub>3</sub> and RbSiH<sub>3</sub>,<sup>10</sup> SiH<sub>3</sub><sup>-</sup> reorientational mobilities for undercooled  $\alpha$ -CsSiH<sub>3</sub>, designated as remnant (i.e.,  $\alpha$ -phase below the approximate 250 K  $\alpha \rightarrow \beta$ phase transition temperature upon cooling) and premonitory (i.e.,  $\alpha$ -phase below the approximate 310 K  $\beta \rightarrow \alpha$  phase transition temperature upon heating) according to the nomenclature from ref 10, show no deviations from the expected temperature-dependent bulk  $\alpha$ -phase mobilities. This makes sense, since anion mobilities are mainly dictated by the local details of their near-neighbor environment. If the local structure of bulk  $\alpha$ -phase is present in the undercooled region, either as a few unit cells or as large crystallites, the associated anion dynamics will be the same. Without further corroborating structural information, one might be tempted to label the *i*-CsSiH<sub>3</sub> phase itself as an undercooled  $\alpha$ -phase (i.e., with a reduced local cubic unit cell constant but nanocrystalline and invisible to diffraction), although again (unlike for KSiH<sub>3</sub> and  $RbSiH_3$ ),<sup>10</sup> there is no distinction found between remnant and premonitory SiH<sub>3</sub><sup>-</sup> anion mobilities. Alternatively, *i*-CsSiH<sub>3</sub> might represent a different more coarsely crystalline intermediate phase, maybe even analogous to the reported intermediate triclinic  $\beta'$ -RbSiH<sub>3</sub> phase,<sup>10</sup> although the intermediate anion mobility would again certainly require a structure with an intermediate unit cell volume. We will assess these possibilities later in the paper based on temperaturedependent NPD measurements of CsSiD<sub>3</sub>.

To see if there was also some analogous intermediate dynamic present for another silanide besides  $CsSiH_3$ , we

performed one high-resolution (30  $\mu$ eV fwhm) QENS measurement on RbSiH<sub>3</sub> on the DCS spectrometer at 281 K, after cooling  $\alpha$ -RbSiH<sub>3</sub> from 300 K. Again, a reasonable spectral fit required two Lorentzian components with order-ofmagnitude-different widths in addition to an elastic peak component and a flat background, which already adequately included the very broad overdamped phonon scattering over the limited energy range considered (see Figure S5). On the basis of the calculated fundamental jump correlation frequencies  $\tau_1^{-1}$  for these two components, it was evident that the dominant broader Lorentzian component yielding a higher  $\tau_1^{-1}$  value of the order  $10^{12} \text{ s}^{-1}$  was reflective of bulk  $\alpha$ -RbSiH<sub>3</sub>.<sup>10,13</sup> On the other hand, a  $\tau_1^{-1}$  value of the order 5 × 10<sup>10</sup> s<sup>-1</sup> corresponding to the narrower Lorentzian component (which was roughly 10% as intense as the broader component) was again too large to be attributed to the  $\beta$ -RbSiH<sub>3</sub> phase and thus must correspond to some type of unknown intermediate structural arrangement. The two  $\tau_1^{-1}$  values are plotted with the CsSiH<sub>3</sub> data in Figure 4. Noting the fairly close proximity of the jump correlation frequency for the intermediate phase to an extrapolation of the jump frequencies for the  $\beta$ -RbSiH<sub>3</sub> phase in Figure 4, we speculate that it may be reflecting the presence of some small fraction of  $\beta$ -like triclinic  $\beta'$ -RbSiH<sub>3</sub> phase, although there is no structural or other evidence supporting its presence upon cooling  $\alpha$ -RbSiH<sub>3</sub> from 300 K. In light of the results of this intriguing RbSiH<sub>3</sub> measurement and the lack of any other comparable high-resolution OENS measurements, it would likely be worthwhile to perform more detailed high-resolution QENS experiments in the future on both KSiH<sub>3</sub> and RbSiH<sub>3</sub> in the transitional temperature region to more fully map out the behavior of any such lower-mobility species.

The activation energies  $E_a$  obtained from the slopes of the linear fits in Figure 4 are presented in Table 1. The  $E_a$  values of 39(1), 33(1), and 32(3) meV, respectively, for the three  $\alpha$ -MSiH<sub>3</sub> (M = K, Rb, and Cs) phases reported previously from refs 9 and 13 were determined by ignoring any potential additional "contamination" broadening from a narrower *i*-phase-related Lorentzian component. This may or may not be so consequential for  $\alpha$ -KSiH<sub>3</sub> or  $\alpha$ -RbSiH<sub>3</sub>, but for the current higher-resolution  $\alpha$ -CsSiH<sub>3</sub> data in Figure 4, the inclusion of a second *i*-phase-related component in the analysis results in a 50% higher  $E_a$  value of 48(2) meV.

The QENS data for *i*-CsSiH<sub>3</sub> in Figure 4 led to a fitted  $E_a$ value of 89(2) meV, which lies between the corresponding values of 105(2) and 48(2) meV for the respective  $\beta$ -CsSiH<sub>3</sub> and  $\alpha$ -CsSiH<sub>3</sub> phases. The intermediate values for both activation energies and anion reorientational jump frequencies are reasonable from a steric viewpoint if the *i*-phase actually possesses a unit-cell volume per MSiH<sub>3</sub> formula unit that is intermediate between those for the  $\beta$ -CsSiH<sub>2</sub> and  $\alpha$ -CsSiH<sub>2</sub> phases. Of course, confirming such structural details with any diffraction-based probe would require the *i*-phase to attain adequately large crystallite domain sizes, which is a topic again assessed later in the paper in light of our NPD measurements. Yet, even without structural measurements, we show in the next section that a comparison of the corresponding SiH<sub>3</sub><sup>-</sup> reorientational mechanisms proposed from QENS measurements for the three different phases can provide further insights concerning the nature of the *i*-phase.

Anion Reorientational Mechanisms. Mechanistic insights concerning the  $SiH_3^-$  reorientational dynamics associated with the different phases of these compounds can be deduced from the Q-dependence of the relative fractions of elastic and quasielastic scattering intensities. This information is typically conveyed by the elastic incoherent structure factor (EISF), which is defined at any Q value as the ratio of elastic to total (elastic+quasielastic) scattering intensities. Figure 7 compares the experimental EISF values with hypothetical curves derived for various different SiH<sub>3</sub><sup>-</sup> reorientation models detailed in the Supporting Information.



Figure 7. Elastic incoherent structure factor (EISF) data vs Q for  $\alpha$ -CsSiH<sub>3</sub> (orange circles, 270 K), *i*-CsSiH<sub>3</sub> (filled blue triangles (cooling)/open blue triangles (heating), 240 K),  $\beta$ -CsSiH<sub>3</sub> (open green stars, 200 K),  $\beta$ -RbSiH<sub>3</sub> (open dark green pentagons, 247 K), and  $\beta$ -KSiH<sub>3</sub> (open blue squares, 292 K). EISFs for  $\alpha$ -CsSiH<sub>3</sub> and *i*-CsSiH<sub>3</sub> were derived from DCS measurements (2.75 and 4.8 Å neutrons), while those for  $\beta$ -KSiH<sub>3</sub>,  $\beta$ -RbSiH<sub>3</sub>, and  $\beta$ -CsSiH<sub>3</sub> from HFBS measurements. Open red star symbol denotes the EISF value for  $\beta$ -CsSiH<sub>3</sub> from NSE measurements at 140 K and Q = 0.8 Å<sup>-1</sup>. EISF model curves for various anion reorientational mechanisms are shown for comparison: (a) 3-fold jumps around the nominal anion  $C_3$ symmetry axis, (b) rotational diffusion around the  $C_3$  axis, (c) 24-site model involving 3-fold jumps around eight differently aligned anion  $C_3$  axes, (d) uniaxial rotational diffusion around eight differently aligned anion  $C_3$  axes, and (e) isotropic rotational diffusion (see the Supporting Information for further model details).

The SiH<sub>3</sub><sup>-</sup> anion reorientations for all  $\beta$ -phase compounds are crystallographically restricted by symmetry to follow a three-site jump model in which H atoms reorient by  $120^{\circ}$ jumps about the nominal 3-fold SiH<sub>3</sub><sup>-</sup> symmetry axis with an average H–H jump distance of  $\approx 2.23$  Å.<sup>3</sup> To have a reasonable agreement between the experimental data and this model, a fraction of immobile H atoms had to be included in all cases as extra elastic-peak intensity, e.g., (30%) for  $\beta$ -KSiH<sub>3</sub> at 292 K, (10%) for  $\beta$ -RbSiH<sub>3</sub> at 247 K, and (43%) for  $\beta$ -CsSiH<sub>3</sub> at 200 K. Extra elastic-peak contributions are to be expected, most certainly reflecting "contamination" due to (i) the elasticscattering fraction from much-more-highly mobile SiH<sub>3</sub> anions associated with coexisting *i*-phases and  $\alpha$ -phases, and (ii) additional elastic-scattering contributions from immobile H atoms associated with other minor hydrogenous impurity phases. Coexisting MSiH<sub>3</sub> phases and other minor impurities such as MH are common in synthesized MSiH<sub>3</sub> compounds as borne out in this and previous studies.<sup>1,3,10,13</sup> Although the high-resolution HFBS measurements will detect the associated elastic scattering from the extra *i*-phases and  $\alpha$ -phases, the fraction of extremely broad quasielastic scattering that would normally be observable with the DCS spectrometer will remain largely outside the HFBS measurement window and invisible as part of the HFBS flat background. This uniaxial reorientational behavior is consistent with the additional higherresolution NSE measurements performed on  $\beta$ -CsSiH<sub>3</sub> at the relatively low temperature of 140 K after heating from 4 K (see Figure S2), where the amounts of coexisting *i*-phase and  $\alpha$ phase and their concomitant excess elastic-peak contributions will be minimal.

We point out that, although it would be preferable to measure the  $\beta$ -phase EISFs out to higher Q values than shown in Figure 7 to more clearly corroborate the rise in EISF values with increasing Q values above 2 Å<sup>-1</sup> as expected for a 3-fold reorientational jump mechanism, we are limited by the HFBS spectrometer to Q values less than  $\approx 1.7$ Å<sup>-1</sup>. Nonetheless, the observed Q-independent quasielastic linewidths in Figure 3 for the  $\beta$ -phase compounds provide an independent confirmation for such a reorientational model.

In contrast to the uniaxial 3-fold jump model describing the  $\beta$ -phase SiH<sub>3</sub><sup>-</sup> reorientations, the  $\alpha$ -phase SiH<sub>3</sub><sup>-</sup> reorientations have been successfully described by a three-dimensional "24site" model established previously,13 which utilizes the 24 positions of a corner-truncated cube as jump locations for H atoms, mimicking the various partially occupied H positions shown in Figure 1. This model represents a composite mechanism comprised of both 3-fold uniaxial reorientations of H atoms around the anion  $C_3$  axis and the 8-fold flipping of this axis itself toward orientations that are aligned along the body diagonals of the cubic Fm-3m unit cell. When considering this model, it is not unreasonable to assume that the anion actually uses its center of gravity as the (three-dimensional) reorientational pivot point, which is on the anion  $C_3$  axis but offset toward the three H atoms by about 0.08 Å from the Si atom center (see Figure S4). If one further assumes that this pivot point (and not Si) is anchored at the high-symmetry Si position determined from refinement of the diffractionaveraged cubic  $\alpha$ -phase structure,<sup>3</sup> then the effective radius of the sphere surface visited by the three H atoms via a 24-site model is slightly smaller than the Si–H bond distance of  $\approx 1.52$ Å established from pair distribution functions for  $\alpha$ -KSiD<sub>3</sub> and  $\alpha$ -RbSiD<sub>3</sub> extracted from neutron total scattering data.<sup>11</sup> Rather, it is more in line with an "effective" Si-H bond distance of ≈1.47–1.49 Å determined by Rietveld refinement of  $\alpha$ -MSiD<sub>3</sub> NPD data.<sup>3</sup> Of course, this refined distance is measured from the average Si high-symmetry position at the center of the cube of eight surrounding alkali metal cations. In reality, the Si atom may actually be slightly off-center by  $\approx 0.08$ Å at any one of eight positions along the body diagonals. Indeed, the characteristically large NPD-derived atomic displacement parameters observed for Si in the  $\alpha$ -phases compared to those for Si in the  $\beta$ -phases<sup>3,10</sup> are consistent with the existence of multiple off-center Si positions in the  $\alpha$ -phases rather than perfectly centered Si atoms.

In line with the above discussion, we used the 24 H positions (extending radially 1.49 Å from the average Si high-symmetry position) for the  $\alpha$ -CsSiH<sub>3</sub> 24-site-model analyses based on the NPD-derived  $\alpha$ -CsSiH<sub>3</sub> structural model.<sup>3</sup> As for  $\alpha$ -KSiH<sub>3</sub> and  $\alpha$ -RbSiH<sub>3</sub><sup>13</sup> this model, rather than one based on

fully isotropic rotational diffusion, fits the  $\alpha$ -CsSiH<sub>3</sub> data well in the temperature range from 350 to 270 K (see Figure S6) after the experimental data are corrected for extra elastic scattering from an immobile fraction (14%) of H atoms from minor hydrogenous impurity phases such as CsH as well as any trace amounts of lingering  $\beta$ -CsSiH<sub>3</sub> (and/or intermediate *i*-CsSiH<sub>3</sub>) phase(s). A similar magnitude correction (10%) was also previously necessary to attain better agreement with the 24-site model for  $\alpha$ -KSiH<sub>3</sub> and  $\alpha$ -RbSiH<sub>3</sub>.<sup>13</sup> Similar to our earlier justifications for the extra elastic scattering in the  $\beta$ phase QENS data, the presence of lingering  $\beta$ -MSiH<sub>3</sub> and minor MH impurity phases in the  $\alpha$ -MSiH<sub>3</sub> phases have also been observed by prior diffraction studies.<sup>1,3,10</sup>

This 24-site model for  $\alpha$ -CsSiH<sub>3</sub>, which reflects 3-fold reorientations of the H atoms around the eight possible crystal alignments of the SiH<sub>3</sub><sup>-</sup>  $(C_3)$  axis of rotation, can be extended to consider more disordered uniaxial rotational diffusion around each differently aligned axis. Over the Q-range of these measurements, this can be well-approximated by merely considering 6-fold  $(60^\circ)$  jumps around each of the axes, instead of 3-fold (120°) jumps, thus doubling the number of possible locations to consider. The details for determining the associated EISF can be found in the Supporting Information, and it is plotted in Figure 7 and Figure S6 for comparison with the experimental data. It is clear that there are only minor differences between the 24-site model and this more disordered model, which could be largely compensated for by very minor corrections (on the order of a percent) in the assumed immobile fraction of elastically scattered H present. Hence, although the 24-site model is simpler and seems sufficient to describe the anion reorientational behavior over our Q-range, we cannot rule out that we are actually observing an  $\alpha$ -phase mechanism involving something closer to uniaxial rotational diffusion rather than 3-fold reorientations around the eight differently aligned axes.

Finally, the EISF behavior of the narrower DCS Lorentzian component associated with the *i*-phase, which was additionally included in the fitting of the QENS data of  $\alpha$ -CsSiH<sub>3</sub>, is also exemplified in Figure 7. This *i*-CsSiH<sub>3</sub> phase component is observed in the temperature region from around 280 to 170 K, contributing the maximal (and overwhelming) fraction of the total quasielastic scattering intensity near 240 K (roughly 3- $4\times$  the intensity of the broader  $\alpha$ -phase component) in both heating and cooling regimens. Hence, this was the temperature used to extract the *i*-CsSiH<sub>3</sub> EISF from the DCS data. Starting with the 240 K DCS data (in cooling), where 2.75 Å neutron wavelength measurements were available for a maximal Orange, we already know the Q-dependent quasielastic intensities for the *i*-phase and  $\alpha$ -phase. To derive the *i*-phase EISF, we need to isolate the *i*-phase elastic scattering contribution from the measured total elastic scattering intensity by removing, first, the amount of Q-dependent elastic scattering due to the minor  $\alpha$ -phase fraction based on the amount of corresponding  $\alpha$ -phase quasielastic scattering and assuming that the  $\alpha$ -phase EISF followed the 24-site model, and second, the extra Q-independent elastic scattering from the known 14% hydrogenous impurity fraction determined earlier during the analysis of the pure  $\alpha$ -phase data at highertemperatures. Without considering any further elastic scattering corrections from any trace fraction of coexisting  $\beta$ -phase (which can also be considered as an immobile phase within this DCS resolution window), the resulting *i*-phase EISF is shown in Figure 7. Although, the data agree very well with the

EISF curve corresponding to the uniaxial 3-fold jump model for Q values less than 2  $Å^{-1}$ , there are marked deviations in the higher-Q region. Yet, they do agree remarkably well with the EISF curve corresponding to the uniaxial rotational diffusion model (i.e., more diffuse SiH<sub>3</sub><sup>-</sup> anion reorientations around the nominal  $C_3$  symmetry axis) over all Q values. The agreement at low Q values for both uniaxial reorientation models and the good overall agreement with the uniaxial rotational diffusion model suggests that no further elastic scattering corrections are warranted. If any more elastic scattering corrections were to be made to account for additional trace  $\beta$ -CsSiH<sub>3</sub>, then the resulting *i*-phase EISF data points would approach closer to the EISF curve corresponding to the sphere-tracing 24-site model, but still deviate significantly with respect to the specific Q-dependent behavior expected, no matter how large of an additional correction is considered. On the basis of this observation, it is reasonable to assume that very little  $\beta$ -CsSiH<sub>3</sub> is indeed present.

A similar procedure was used to determine the *i*-phase EISF at 240 K (in heating), but only 4.8 Å neutron wavelength DCS data were available, so the maximum Q value was only 2.35  $Å^{-1}$ . Nonetheless, the resulting data, also shown in Figure 7, favor the same uniaxial rotational diffusion model as for the 240 K data in cooling.

The particular *Q*-dependent behavior (such as the functional shape and position of the first minimum) of the derived EISF for *i*-CsSiH<sub>3</sub> at 240 K (in both cooling and heating) points strongly to a uniaxial reorientational model around the anion  $C_3$  axis as happens in the  $\beta$ -phase rather than a more-threedimensional 24-site-type model as happens in the  $\alpha$ -phase. Yet, it is important to note that the relatively more muted EISF oscillation at higher Q values further suggests that the *i*-CsSiH<sub>3</sub> anion reorientations around the  $C_3$  symmetry axis are more delocalized than strictly 120° jumps, with the data following a uniaxial small-angular-jump rotational diffusion model reasonably well. The true uniaxial mechanism may be something in between 3-fold jumps and rotational diffusion, e.g., a partial angular delocalization of possible H positions at other orientations nearby the main 3-fold positions. This type of delocalization model has been used to address the QENS measurements concerning the reorientations of BH<sub>4</sub><sup>-</sup> anions in hexagonal phase of LiBH<sub>4</sub>.<sup>21</sup> As the extent of this angular "smearing" of jump positions increases from no smearing to complete smearing (i.e., rotational diffusion), the characteristic EISF functional form with Q will gradually transform from the classic 3-fold jump model to the rotational diffusion model. Although some N-dependent variation of the quasielastic line width with Q is expected for N-fold uniaxial jumps above N =3, a uniaxial rotational diffusion model (i.e., small-angular jumps for large N values) is not inconsistent with the muted Qsensitivity of the quasielastic line width seen in Figure 6 over the measured Q-range, according to Bee's analysis<sup>19</sup> of the expected Q-dependence of the composite quasielastic scattering (fwhm) line width for the case of very small angular jumps  $(N \ge 12)$  around a circle. We note that such an intermediate uniaxial rotational diffusion model would be a particularly reasonable progression from a more ordered, uniaxial 3-fold jump model in the  $\beta$ -phase to a less ordered, eight-axis version of uniaxial rotational diffusion (instead of the 24-site model) in the  $\alpha$ -phase.

Nedumkandathil et al.<sup>10</sup> have suggested from the EISF analysis of their QENS data for KSiH<sub>3</sub> and RbSiH<sub>3</sub> that the

SiH<sub>3</sub><sup>-</sup> anions in their remnant undercooled  $\alpha$ -phases undergo uniaxial 3-fold jumps around the  $C_3$  axis. This is somewhat at odds with the more diffuse uniaxial reorientational mechanism deduced here for *i*-CsSiH<sub>3</sub>, although it is not clear at this point if we are interpreting dynamical phenomena from the same type of intermediate species as those identified as remnant undercooled  $\alpha$ -phases in KSiH<sub>3</sub> and RbSiH<sub>3</sub>. Again, higherresolution QENS measurements are ultimately needed across the transition regions for KSiH<sub>3</sub> and RbSiH<sub>3</sub> to better understand the similarities and differences in dynamical behavior among the three MSiH<sub>3</sub> compounds.

It was informative to construct rough phase diagrams for  $CsSiH_3$  (upon both cooling and heating regimens) based on integrated intensity analyses of the DCS QENS spectra with temperature at a single appropriate Q value (0.8 Å<sup>-1</sup> in this case). These are shown in Figure 8. In particular, the phase fractions were estimated at a number of different measured temperatures under the assumption that the total integrated incoherent scattering intensity from all H atoms, which equals



**Figure 8.** Phase diagrams for  $CsSiH_3$  derived from anion dynamical behavior with temperature upon (a) cooling from 350 K and (b) heating from 25 K. The symbols present the calculation of the phase fractions obtained from QENS measurements, while the dashed lines represent guides to the eye.

the summed intensities of all quasielastic and elastic components in the QENS spectra (without the extra intensity from the broad overdamped mode scattering component), is a constant (which is essentially ignoring the minor temperaturedependent effects of the Debye-Waller factor on intensity). Moreover, the molar fraction of each CsSiH<sub>2</sub> phase ( $\alpha$ , *i*, and  $\beta$ ) was assumed to be directly proportional to its total component scattering intensity. It was further assumed that the 24-site model and the uniaxial rotational diffusion model (and their associated EISFs) represent the respective anion reorientational behaviors for the  $\alpha$ - and *i*-phases. The relative fraction of  $\alpha$ - and *i*-phases at any given temperature can then be estimated by determining the total amount of scattering corresponding to each of these phases at  $Q = 0.8 \text{ Å}^{-1}$ . The relative intensities of the quasielastic components for the  $\alpha$ and *i*-phases are obtained from the spectral component fits of the QENS spectrum at this Q value. The corresponding elastic intensities for each phase are then calculated from the respective EISF model values at this same Q value. Next, the total scattering intensity for each of the  $\alpha$ - and *i*-phases is determined by summing the individual elastic and quasielastic component intensities. Finally, the relative fraction of the  $\beta$ phase is determined from the residual elastic scattering intensity left over after subtracting the total scattering intensities due to the  $\alpha$ -phase plus the *i*-phase plus the known impurity elastic scattering from the constant summed total scattering intensity (due to all phase fractions) as determined from the overall spectral component fits of the QENS spectrum mentioned above. This process is then repeated for all measured temperatures. On the basis of this phase diagram for CsSiH<sub>3</sub>, it is obvious that all three phases are indeed present over a broad intermediate temperature region, with a maximum *i*-phase fraction of about 75% to 85% present near 240 K. There appears to be a more pronounced transitional hysteresis occurring in the higher-temperature region between the  $\alpha$ -phase and the *i*-phase than in the lowertemperature region between the  $\beta$ -phase and the *i*-phase, which helps to better understand the observed hysteresis due to changing mechanism and phase-fraction effects in the higher-temperature region of the FWS for CsSiH<sub>3</sub> in Figure S1.

CsSiD<sub>3</sub> Temperature-Dependent Structural Behavior. After establishing the QENS-derived CsSiH<sub>3</sub> phase diagrams in Figure 8, it was highly informative to compare them to the temperature-dependent structural evolution of CsSiD<sub>3</sub> phases via NPD. Figure 9 displays a subset of NPD patterns collected at progressively lower temperatures upon cooling from 299 K down to 162 K. (N.B., no NPD measurements were performed upon heating.) Ignoring any extremely subtle changes, e.g., such as a monoclinic to triclinic transformation analogous to that reported for  $\beta$ -RbSiD<sub>3</sub>,<sup>10</sup> there are no obvious signs of an additional long-range-ordered phase at the intermediate temperatures between the  $\alpha$ - and  $\beta$ -phases, only a slight drop of roughly 15% in the apparent mass of crystalline material in the transition region, as might typically be expected to accompany such a dramatic phase change. In particular, we took all of the NPD patterns collected and generated a rough phase diagram plot in Figure 10 (analogous to those generated in Figure 8) by evaluating the areas under selected Bragg peaks as functions of temperature. The (200) reflection was chosen for the  $\alpha$ -phase and the (301) + (202) reflections were chosen for the  $\beta$ -phase. The integrated peak intensities corresponding to each phase were normalized so that the values were unity at 299 K for the  $\alpha$ -phase and at 162 K for the  $\beta$ -phase. Done in



**Figure 9.** NPD patterns for  $CsSiD_3$  upon cooling from 299 to 162 K, indicating pertinent lattice reflections for the  $\alpha$ -phase (top), which is the stable phase at the higher temperatures, and for the  $\beta$ -phase (bottom), which is the stable phase at the lower temperatures.



**Figure 10.** Evolution of the normalized NPD Bragg peak intensities for  $\alpha$ -CsSiD<sub>3</sub> (yellow) and  $\beta$ -CsSiD<sub>3</sub> (green) with temperature upon cooling. Blue symbols represent the extra peak intensities at each temperature that must be added to the summed intensities for the  $\alpha$ and  $\beta$ -phases to attain unity.

this way, the normalized peak intensities could also be considered as a measure of the phase fractions of the crystalline portion of the CsSiD<sub>3</sub>. By summing the  $\alpha$ - and  $\beta$ phase fractions at each temperature, we could then deduce the extra fraction required to attain unity. This extra fraction

approximates the loss of crystalline material during the phase transformation potentially due to a marked decrease in coherence lengths for a portion of this affected material and/ or the nucleation of nanosized domains of a structurally distinct intermediate phase with local geometric arrangements that are different than (and intermediate to) those for the  $\alpha$ - and  $\beta$ -phases.

Although we anticipate that  $CsSiD_3$  will display minor temperature-related deviations in phase-transition behavior compared to  $CsSiH_3$  with respect to the exact position and breadth of the transition region, it is reasonable to assume that  $CsSiD_3$  and  $CsSiH_3$  will be morphologically similar, allowing for a meaningful comparison of Figures 8 and 10. The missing fraction of crystalline  $CsSiD_3$  material in Figure 10 is akin in thermal evolution to that of the *i*-phase fraction of  $CsSiH_3$ material in Figure 8a, although the overwhelming magnitude (roughly 85%) observed for the latter  $CsSiH_3$  fraction at 240 K is over 5-fold higher than that for the former  $CsSiD_3$  fraction.

One must keep in mind that, although NPD senses only the coarser crystalline portion of the CsSiD<sub>3</sub>, QENS is a highly local probe and detects all of the SiH<sub>3</sub><sup>-</sup> anions in the CsSiH<sub>3</sub>, irrespective of crystallite size, so it provides a global tally of the anion dynamics. Even if these intermediate fractions in both figures happen to represent the same type of dynamically distinct, intermediate structural arrangements, the large discrepancy in phase fractions can only be reconciled if one assumes that (i) the CsSiH<sub>3</sub> is comprised predominantly of short-coherence-length nanodomains largely invisible to diffraction, with a minority of longer-coherence-length crystalline material, and (ii) the *i*-CsSiH<sub>3</sub> phase forms chiefly within these nanocrystalline domains, both upon cooling from the nano- $\alpha$ -phase and upon heating from the nano- $\beta$ -phase, and remains stabilized over an extended intermediate temperature range. For the diffraction-visible, more coarsely crystalline material, Figure 10 indicates a more abrupt transition from  $\alpha$ -phase to  $\beta$ -phase, largely bypassing the stabilization of a similar intermediate structural arrangement extending down to lower temperatures as observed for the nanocrystalline fraction, before ultimately forming the  $\beta$ -phase. Depending on the exact nature (i.e., short-coherence-length  $\alpha$ -,  $\beta$ -, or *i*-phase) of the 15% amorphous-like material inferred by the CsSiD<sub>3</sub> NPD measurements in the intermediate temperature regime, the fraction of the shorter-range-ordered CsSiH<sub>3</sub> nanocrystallites present in the CsSiH<sub>3</sub> over the entire temperature range is estimated to be anywhere between 70% to 85%.

The existence of such a large fraction of amorphous-like nanomaterial is also fully consistent with the unusually large amount of diffuse scattering intensity, i.e., an order of magnitude more than the intensity under the NPD Bragg peaks, as highlighted for both  $\alpha$ -CsSiD<sub>3</sub> and  $\beta$ -CsSiD<sub>3</sub> in Figure S7. Moreover, instead of being fairly flat, the diffuse scattering background exhibits a rather dramatic broad hump that peaks in the Q region corresponding to what would be expected if the form factor were dominated by a single SiD<sub>3</sub><sup>-</sup> anion. In reality, the diffuse background is rather smeared out since the nanodomains will have a distribution of short coherence lengths, i.e., a broad distribution of different small unit-cell clusters to consider, although the hump is still an indication that the basic SiD3<sup>-</sup> geometric arrangement (and more specifically, the three D atoms) dominates the Q dependence. This diffuse scattering behavior can also be seen in past NPD patterns for KSiD<sub>3</sub> and RbSiD<sub>3</sub>,<sup>3</sup> which may signal

that nanodomain formation is a general phenomenon occurring in these compounds during their synthesis. It would be interesting to see if one could somehow reduce the amount of nanomaterial in  $CsSiH_3$  by, e.g., using different synthesis methods or prolonged higher-temperature annealing under  $H_2$  pressure. Then it should be possible to mitigate the formation of the *i*-phase during temperature cycling.

#### 

QENS measurements were employed to gain deeper insights into the dynamical behavior of the SiH3<sup>-</sup> anions in the lowtemperature ordered  $\beta$ -phases and the high-temperature disordered  $\alpha$ -phases of the monoalkali silanides (MSiH<sub>3</sub>, where M = K, Rb, and Cs), which have been recently proposed as possible materials for near-ambient hydrogen-storage systems. The results show that the  $\beta - \alpha$  phase transition leads to dynamical changes corresponding to orders of magnitude more rapid reorientational motions of the pyramidal anions. Maximum jump frequencies of the  $\beta$ -phase anions near the  $\beta - \alpha$  transitions vary from around  $10^9 \text{ s}^{-1}$  for  $\beta$ -KSiH<sub>3</sub> to  $10^{10} \text{ s}^{-1}$  and higher for  $\beta$ -RbSiH<sub>3</sub> and  $\beta$ -CsSiH<sub>3</sub>. Focusing on CsSiH<sub>3</sub> in and above this transition region, we observe that the expanded and disordered  $\alpha$ -CsSiH<sub>3</sub> compound exhibits significantly higher anion reorientational jump frequencies approaching and exceeding  $10^{12}$  s<sup>-1</sup>, in accordance with prior QENS results. The lower anion mobilities in the ordered  $\beta$ -phases compared to the disordered  $\alpha$ -phases are expected, due to the smaller (more sterically restrictive) unit cell volumes for the former. In contrast to the  $\beta$ -phases, which show significantly higher reorientation activation energies and larger deviations between different MSiH<sub>3</sub> compounds, relatively weaker temperature dependences of anion reorientational jump frequencies are observed for the  $\alpha$ -phases with smaller differences in activation energies between the different congeners.

The single crystallographic orientations for each SiH<sub>3</sub><sup>-</sup> anion in the ordered  $\beta$ -phases point to only one physically reasonable anion reorientational mechanism, i.e., uniaxial 3-fold rotational jumps of the H atoms around the anion 3-fold symmetry axis. The SiH<sub>3</sub><sup>-</sup> reorientations in the disordered  $\alpha$ -CsSiH<sub>3</sub> are adequately modeled by H jumps between 24 different jump locations distributed radially around the anion center of gravity, in line with the various H-site occupations determined from NPD, although we cannot rule out a more disordered model involving uniaxial rotational diffusion around the various possible crystal alignments of the anion  $C_3$  symmetry axis. The unusual nature of the anion dynamical transformation upon transitioning between the  $\alpha$ - and  $\beta$ -phases of CsSiH<sub>3</sub> was probed in more detail, corroborating the presence of a dynamically distinct intermediate phase (i.e., our i-phase), which may possibly be related to the nanosized "undercooled  $\alpha$ -phase" KSiH<sub>3</sub> and RbSiH<sub>3</sub> recently reported by Nedumkandathil et al. The comprehensive QENS results for CsSiH<sub>3</sub> suggest that the SiH3<sup>-</sup> anions associated with this *i*-phase possess an order-of-magnitude lower orientational mobility than that for  $\alpha$ -phase anions (though an order-of-magnitude higher orientational mobility than that for  $\beta$ -phase anions), as well as a decreased reorientational dimensionality within the neutron resolution window to uniaxial small-angular jumps rather than something more akin to the three-dimensional  $\alpha$ phase anion motions. Although these dynamical and mechanistic details elucidated by QENS cannot by themselves provide any more definite insights concerning local structural

symmetry of the *i*-phase, they suggest nonetheless that it possesses a unit cell volume per CsSiH<sub>3</sub> formula unit somewhere between those for the  $\alpha$ - and  $\beta$ -phases. In such an intermediate-sized unit cell, there is more anion space for more rapid uniaxial reorientations than in the  $\beta$ -phase but not enough anion space to enable noticeably rapid three-dimensional 8-fold realignments of the anion  $C_3$  axis as for the  $\alpha$ -phase.

Finally, the combination of these QENS results for CsSiH<sub>3</sub> with complementary NPD results for CsSiD<sub>3</sub> strongly suggest that this structurally and dynamically distinct *i*-phase is chiefly associated with short-range-ordered nanodomains (invisible to diffraction), which dominate the CsSiH<sub>3</sub> sample. This is particularly interesting from a thermodynamics viewpoint, since it indicates that decreasing the coherence length toward the nanoregime enables the stabilization of a local structural arrangement over an extended temperature range for CsSiH<sub>3</sub> that is intermediate to the structural arrangements of the  $\alpha$ and  $\beta$ -phases. For more coarsely crystalline domains, the NPD results suggest a sharper transition region between  $\alpha$ - and  $\beta$ phases, although it is not yet clear if the apparent minor loss of crystallinity associated with these domains in the transition temperature region can be equated to the formation of any comparable *i*-phase-like nanodomains.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b08257.

Complementary QENS and NPD data, SiH<sub>3</sub><sup>-</sup> schematic, and details of EISF models (PDF)

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