Probing structure-dependent reorientational behavior of SiH_3^- anions in alkali-metal silanides by quasielastic neutron scattering

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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. 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 for all three alkali-metal compounds due to an enthalpy–entropy compensation effect, i.e., as the cation size increases, there are simultaneous linear increases in the enthalpy (more stable silanide) and entropy changes (more localized H atoms in the crystal structure). Hence, the dynamical nature of the H atoms in the various $MSiH_3$ compounds is of interest from an entropic viewpoint. All $MSiH_3$ compounds undergo hysteretic phase transitions upon heating and cooling between ordered monoclinic or orthorhombic β-phase structures to disordered face-centered-cubic α-phase structures (see Figure 1). In contrast to crystallographically ordered β-phase SiH_3^- anions, the α-phase anions exhibit three-dimensional orientational disorder. Previous quasielastic neutron scattering (QENS) results for all three α-phase compounds indicated decreasing SiH_3^- reorientational mobility (increasing order) with increasing cation size [1,2], which is qualitatively consistent with the observed compensation effect. Here, QENS measurements on the DCS, HFBS, and NSE spectrometers over a wide range of resolutions were used to fully characterize the alkali-metal-dependent anion reorientational dynamics in the ordered β-$MSiH_3$ compounds as well as the unusual nature of the rotator-phase transition between the β-phases and α-phases for $CsSiH_3$ [3].

The QENS data in Figure 2 show that the anion reorientational mobility in the β-phases trends dramatically higher with increasing cation size, which is opposite to what was observed in the α-phases, but makes sense from a purely steric perspective (i.e., lattice volume to accommodate the SiH_3^- anion increases with increasing cation size). Maximum jump frequencies of the β-phase anions near the β-α transitions range from around 10^9 s^{-1} for β-$KSiH_3$ to 10^{10} s^{-1} and higher for β-$RbSiH_3$ and β-$CsSiH_3$. Due to the ordered nature of the β-phase lattice, the anions are effectively restricted to undergo only uniaxial three-fold rotational jumps around the anion quasi-C_3 symmetry axis, which is consistent with the observed behaviors of the β-phase elastic incoherent structure factors (EISFs) in Figure 3.

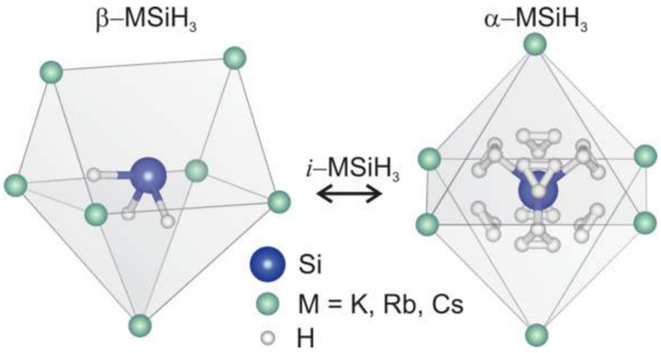

FIGURE 1: Structural differences between the ordered β-$MSiH_3$ and disordered α-$MSiH_3$ (M = K, Rb, Cs) phases showing the respective near-neighbor cation environments surrounding the pyramidal SiH_3^- anions. The multiple H atoms distributed radially around the Si atom represent all of the possible H positions associated with the orientationally disordered SiH_3^- anions in this structure. *i*-$MSiH_3$ denotes the possible formation of 'intermediate" phases in the transition regions.

$CsSiH_3$ was the focus of further studies to map out the evolving anion dynamical behavior at temperatures above the β-phase region. As in α-$KSiH_3$ and α-$RbSiH_3$, the highly mobile anions (with reorientational jump frequencies approaching and exceeding 10^{12} s^{-1}, see Figure 2) in the disordered α-$CsSiH_3$ are all adequately modeled by H jumps between 24 different locations distributed radially around the anion center of gravity (see Figure 3), although even higher anion reorientational disorder cannot be ruled out. QENS data for $CsSiH_3$ in the transition region between the α- and β-phases corroborated the appearance of dynamically distinct intermediate (*i*-) phases. The associated SiH_3^- anions possess orientational mobilities that are an order-of-magnitude lower than those for α-phase anions but also an

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order-of-magnitude higher than those for β-phase anions (see Figure 2). These anions appear to undergo uniaxial small-angular-jump reorientations that are more akin to the lower-dimensional β-phase anion motions rather than to the multi-dimensional α-phase anion motions (see Figure 3). 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 $CsSiH_3$. Figure 2 depicts the hysteretic $CsSiH_3$ phase diagrams in heating and cooling regimens derived solely from the temperature-dependent QENS measurements for the various component phases.

These QENS results for $CsSiH_3$ bolster the previous observation for $KSiH_3$ and $RbSiH_3$ [4] that distinct nanosized intermediate phases exist and exhibit anion orientational mobilities intermediate between those for the α- and β-phases. Determining the exact structural nature of these *i*-phase nanodomains will require further investigation.

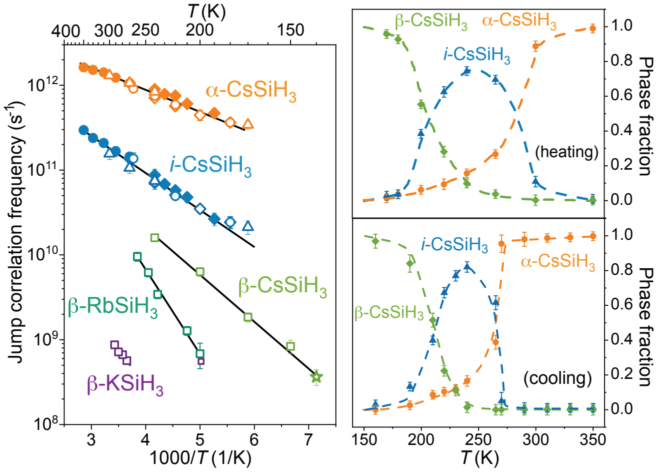

FIGURE 2: (left) Anion jump correlation frequencies τ_1^{-1} vs. 1/*T* for various $MSiH_3$ phases as determined from measurements on DCS (circles, diamonds, triangles, and pentagons), HFBS (squares), and NSE (stars) spectrometers. Filled and open symbols indicate measurements during cooling and heating regimens, respectively. (right) 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.

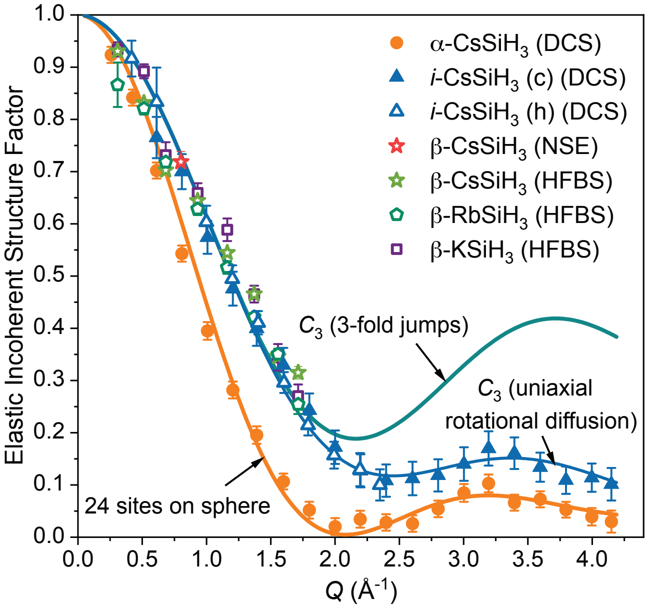

FIGURE 3: Elastic incoherent structure factor (EISF) data vs. *Q* (using various spectrometers) for α-$CsSiH_3$ (270 K), *i*-$CsSiH_3$ (cooling (c)/heating (h), 240 K), *β*-$CsSiH_3$ (green, 200 K; red, 140 K), *β*-$RbSiH_3$ (247 K), and *β*-$KSiH_3$ (292 K). EISF model curves for various reorientational mechanisms are shown for comparison.

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