

^{29}Si NMR study on the stoichiometry of the silicon clathrate $\text{Na}_8\text{Si}_{46}$

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The ^{29}Si magic angle spinning NMR spectrum of $\text{Na}_8\text{Si}_{46}$ exhibits three resonances with large positive Knight shifts assigned to the inequivalent (16i, 6c, and 24k) Si sites in the structure. The integrated intensities are in the ratio $[15.7 \pm 0.3]:[6.5 \pm 0.6]:[23.8 \pm 0.5]$. Along with Rietveld refinement of site occupancies, this result demonstrates that the compound is the stoichiometric clathrate $\text{Na}_8\text{Si}_{46}$, rather than an intermetallic Zintl compound containing silicon vacancies. The result is important for interpreting superconducting and thermoelectric characteristics of members of the tetrelide clathrate family. [S0163-1829(99)00842-5]

Group IV (Si, Ge, Sn) tetrelide clathrate compounds (TC's) (Ref. 1) have been receiving increasing attention due to the discovery of superconductivity ($T_c \sim 4$ K) in the Na-Ba-Si₄₆ series,² and by the recognition that their low thermal conductivity and high Seebeck coefficient render them promising thermopower materials for solid-state refrigeration applications.³ There is also speculation that the predicted wide band gaps of these materials could render them as useful optical materials.⁴ The TC's are structurally analogous to ice clathrate hydrates, formed by cagelike structures of water molecules around included gas or solvent molecules. The fullerene-like structural units consist of polyhedra defined by five- and six-membered rings. The TC network consists of tetrahedrally coordinated Si, Ge, or Sn, with alkali or alkaline-earth metals (M) within the cages. Two Si clathrate structures identified to date: $M_x\text{Si}_{46}$ ($x_{\text{max}}=8$) and $M_y\text{Si}_{136}$ ($y_{\text{max}}=24$), are the analogs of clathrate hydrates I and II. The structure I compounds of Sn have been shown to bear formulas $M_8\text{Sn}_{44}\square_2$, ($M=\text{K}, \text{Rb}$) where $\square$ represents a vacancy on a framework site.⁵ This stoichiometry shows these clathrates to be ionic Zintl compounds, which are semiconducting or insulating. In contrast, $\text{Na}_8\text{Si}_{46}$ is metallic, indicating that it is better described as a "true" clathrate with close to ideal framework site occupancy, and with the additional electrons contributing to its conduction band. Obtaining a correct description of the stoichiometry and the electron occupancy is thus critical to understanding and predicting the electronic properties of these materials, including superconductivity and their thermopower characteristics. One of the most remarkable differences between compounds with vacancies and ones without is that the former are semiconducting and the latter are semimetallic. The immediate implica-

tion of this observation can be seen from the functional form of the so-called figure of merit (ZT) that quantifies thermoelectric efficiency:

$$ZT = \alpha^2 \sigma T / \kappa.$$

Here α , σ , κ are, respectively, the Seebeck coefficient, the electrical conductivity, and thermal conductivity of the material and T the absolute temperature. Within this framework, metals are poor candidates owing to their low Seebeck coefficients and the limited σ/κ ratio. Insulators, on the other hand, have large Seebeck coefficients and low thermal conductivities, but are limited by their poor electrical conductivities.⁶ Thus semiconducting materials midway between metals and insulators are desired. Semiconducting clathrates have the additional advantage that the "rattling" of guest atoms in the cages can reduce the thermal conductivity component in these materials. This has been the motivation for Slack's introduction of the *phonon glass electron crystal* (PGEC, Ref. 3) concept and subsequent experiments on clathrates based on this idea. Vacancies thus provide as useful "knobs" for tuning the transport properties of these materials. Solid-state magic angle spinning (MAS) ^{29}Si NMR is an ideal probe of both the framework site occupancy and the nature of Si contributions to the electronic states near the Fermi level. We present here results of a ^{29}Si MAS NMR study of $\text{Na}_8\text{Si}_{46}$ combined with Rietveld refinement of x-ray-diffraction data that demonstrate the full framework site occupancy, combined with a pseudopotential local-density approximation (LDA) study of the band structure in the region of the Fermi level that supports our findings and allows interpretation of the observed NMR shifts.

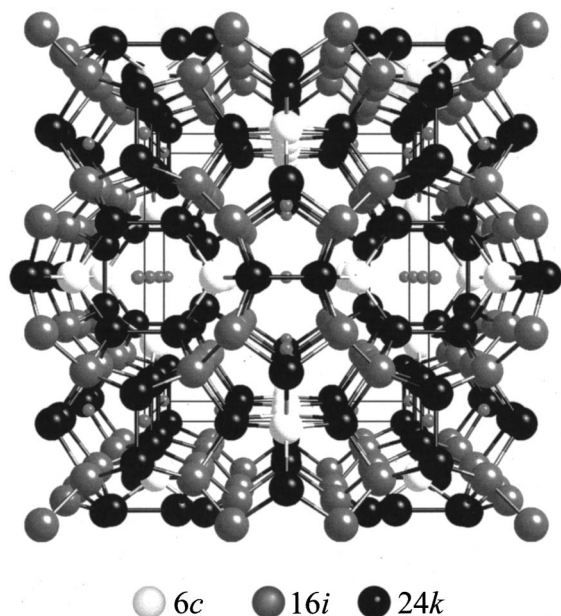


FIG. 1. The structure I clathrate $\text{Na}_8\text{Si}_{46}$ shown along [100] direction. The three inequivalent crystallographic sites 6c, 16i, and 24k are shown in varying shades of black. The guest atoms (Na, Ba, etc., shown as smaller spheres) “reside” at the center of the cages formed by silicon. X-ray analysis shows no vacancies in the structure. A quantitative ^{29}Si NMR corroborates this finding. This structure is an isomorph of the naturally occurring clathrate hydrate I, and the silicate melanophlogite.

The structure of $\text{Na}_8\text{Si}_{46}$ (space group $Pm\bar{3}n$) is built up from two smaller dodecahedra (Si_{20}) and six larger tetrakaid-ecahedra (Si_{24}) connected through five-membered rings. The voids in the polyhedra provide the sodium atom sites. The structure contains three inequivalent Si sites (6c, 16i, and 24k, with symmetries $4m2$, 3, and m , and multiplicities of 6, 16, and 24; Fig. 1). Samples of $\text{Na}_8\text{Si}_{46}$ were synthesized by thermal decomposition of the Zintl phase NaSi in vacuum at 375 °C. NaSi was obtained by treating Na and Si in a sealed tantalum capsule at 650 °C.⁷ X-ray-diffraction analysis showed that the sample was essentially phase pure, with <5% w/w (weight %) of the $\text{Na}_x\text{Si}_{136}$ (structure II) phase.

^{29}Si NMR spectra were collected on a 400-MHz Varian Unity spectrometer operating at 9.4 T (Larmor frequency = 79.46 MHz for ^{29}Si). Samples were loaded in a 5-mm silicon nitride rotor set at the magic angle (54.74°) and spun at 12 kHz. Reported ^{29}Si NMR shifts are referenced to tetramethylsilane [TMS: $\text{Si}(\text{CH}_3)_4$]. The spectrum shows three distinct peaks at 617, 653, and 842 ppm, along with their associated spinning side bands (Fig. 2). From inspection of relative peak heights, these resonances are readily assigned to the three inequivalent silicon sites in the structure: 16i, 6c, and 24k, respectively. Integration under the main peaks and their associated side bands following a Lorentzian fitting procedure gave the relative intensity ratios as $[15.7 \pm 0.3]:[6.5 \pm 0.6]:[23.8 \pm 0.5]$, in excellent agreement with the results from a Rietveld analysis of the powder x-ray-diffraction pattern (Fig. 3, Table I). Complete details of the refinement are presented elsewhere.⁷

The magnitude and direction of the ^{29}Si NMR shifts confirm that they are Knight shifts and that the compound is

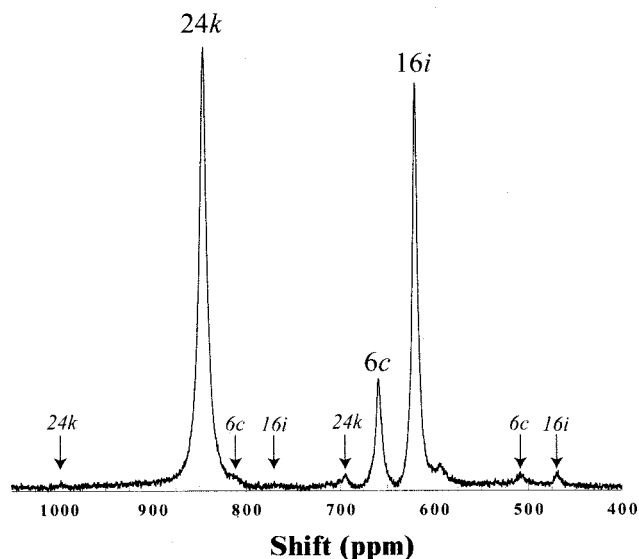


FIG. 2. Room-temperature ^{29}Si MAS NMR spectrum of $\text{Na}_8\text{Si}_{46}$ recorded at an operating field of 9.4 T. The three peaks labeled 6c, 16i, and 24k are such that the corresponding integrated intensities reflect the three inequivalent crystallographic sites in $\text{Na}_8\text{Si}_{46}$ (Fig. 1). For obtaining the total integrated intensity of each site, the corresponding sidebands (arrows with italicized labels) were also accounted for. The small shoulder (at ~ 590 ppm) to the 16i peak is due to a trace of an unidentified impurity (see Ref. 17). Relaxation times were obtained using the standard inversion recovery method. For the sites 6c, 16i, and 24k we obtained T_1 's of 38.1 ± 5.9 , 24.3 ± 0.7 , and 40.0 ± 0.9 ms, respectively.

metallic, as indicated by previous conductivity measurements.¹ NMR shifts of insulating and semiconducting tetrahedrally bound Si compounds occur in the range 0–130 ppm.⁸ The large positive shifts observed for the Si sites in $\text{Na}_8\text{Si}_{46}$ are consistent for a compound with conduction band electrons. This result is also consistent with our previous NMR study of the ^{23}Na atoms in the structure.⁹

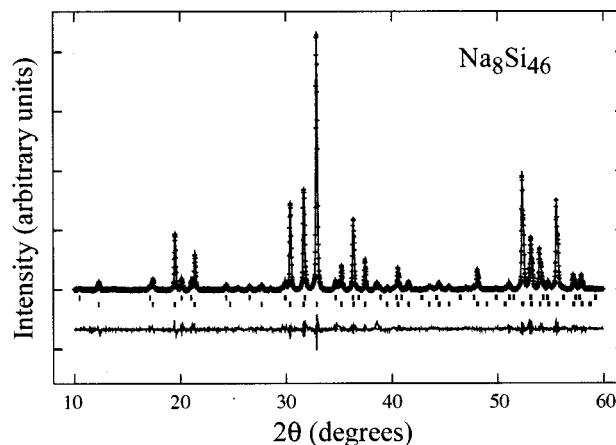


FIG. 3. Rietveld profile fit on x-ray data of $\text{Na}_8\text{Si}_{46}$ (bottom tick marks). In order to check for purity, reflections for $\text{Na}_x\text{Si}_{136}$ were also refined (top tick marks). Experimental data points are shown as plusses (+) and theoretical fits are shown as solid curves. Also shown below the fit is the difference between the observed and theoretical patterns. From the refined site occupancies no vacancies were observed at any of the three crystallographic sites. See Table I for a direct comparison between ^{29}Si NMR and x-ray results.

TABLE I. Selected refinement details for a direct comparison of x-ray and NMR analysis of $\text{Na}_8\text{Si}_{46}$.

Space group $Pm\bar{3}n$; $a = 10.196\,48(2)\text{ \AA}$; $V = 1060\text{ \AA}^3$						
Radiation wavelength: Cu $K\alpha$ $1.5406\text{ \AA}$; 3288 data points						
$\chi^2 = 2.57$; residuals (R_p and R_{wp}) ^a ; 0.0499 and 0.0651						
(samples contained ^b <5% w/w $\text{Na}_x\text{Si}_{136}$)						
Atom	x	y	z	Fraction	Total Si/Na from X-ray analysis	Total Si from NMR analysis
Si1 (6c)	1/4	0	1/2	1.012(8)	6.07 ± 0.05	6.51 ± 0.62
Si2 (16i)	0.1851(1)	0.1851(1)	0.1851(1)	0.997(7)	15.95 ± 0.11	15.74 ± 0.30
Si3 (24k)	0	0.3077(2)	0.1175(2)	0.991(6)	23.78 ± 0.14	23.76 ± 0.48
Na1 (2a)	0	0	0	1.009(8)	2.02 ± 0.02	
Na2 (6c)	1/4	1/2	0	0.989(7)	5.93 ± 0.04	

^a $R_p = \sum |I_{io} - I_{ic}| / \sum I_{io}$, where I_{io} and I_{ic} are the observed and calculated intensities at point i respectively, and $R_{wp} = \{ \sum w_i (I_{io} - I_{ic})^2 / \sum w_i I_{io}^2 \}^{1/2}$, where w_i is the weight assigned at each intensity step.

^bContamination is represented in weight (w/w) percentages (see Ref. 17).

Two Knight shifted lines, with large ^{23}Na NMR shifts of ~ 2000 and ~ 1750 ppm, were observed for Na atoms in the two polyhedral sites. T_1 relaxation times measured using the inversion recovery technique for the 6c, 16i, and 24k Si sites in this study were 38.1 ± 0.7 , 24.3 ± 0.7 , and 40.0 ± 0.9 ms, respectively.

The magnitude of the ^{29}Si Knight shifts K are described by the relationship¹⁰

$$K = \frac{8\pi}{3} \cdot \langle |\psi(r_{\text{Si}})|^2 \rangle \cdot \chi_s^e, \quad (1)$$

where r_{Si} describes the Si nuclear positions, $\langle |\psi(r_{\text{Si}})|^2 \rangle$ indicates an average over the Fermi surface of the absolute square of the electronic wave function with s character evaluated at the positions of the Si nuclei, and χ_s^e is the electronic spin susceptibility which in a simple metal is proportional to the electronic density of states (DOS) at the Fermi level. To investigate trends in the NMR shifts, we computed the site- and angular-momentum-projected DOS using the following procedure. First, we calculated the electronic band structure of $\text{Na}_8\text{Si}_{46}$ within the local-density approximation (LDA), using a plane-wave basis set¹¹ and an efficient ultrasoft pseudopotential.¹² We began by optimizing the framework Si_{46} (i.e., without Na atoms for efficient initial calculation within an insulating system) and found a unit-cell constant $a_0 = 10.10\text{ \AA}$. The Na atoms were then incorporated at the centers of the polyhedra, the structural model scaled to the experimental value for $\text{Na}_8\text{Si}_{46}$ ($a_0 = 10.19\text{ \AA}$), and the band structure recalculated. A plane-wave energy cutoff of 11 Ry was used and the Brillouin-zone integrations were performed using a $2 \times 2 \times 2$ k -space grid in the geometry optimization. A $10 \times 10 \times 10$ k -space grid was chosen to determine the self-consistent charge density which is input for the band-structure calculation.

The resulting total electronic DOS is shown in Fig. 4(a). For calculating the site- and angular-momentum-projected DOS, we projected the wave function onto a spherical harmonic of s symmetry (s DOS) in nonoverlapping spheres encompassing each Na and Si atom. The s DOS contribution at each of the three Si sites is shown in Figs. 4(b)–(d). The results permit us to draw the important conclusion that the s

DOS at the Fermi level at each of the three sites is different, and so there should indeed be a unique NMR signal from each of the sites. The Fermi-level s DOS contribution is largest from Si at the 24k site, so these nuclei ought to have the

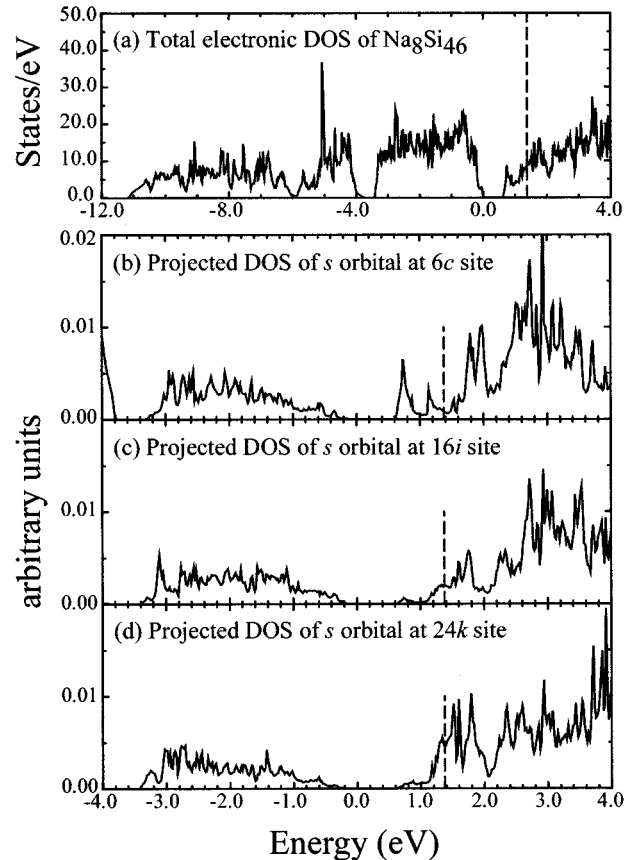


FIG. 4. (a) The total electronic density of states of $\text{Na}_8\text{Si}_{46}$ over all the valence bands and over the lower portion of the conduction bands. The density-functional theory determined s -orbital angular momentum projected density of states at the silicon (b) 6c sites, (c) 16i sites, and (d) 24k sites for $\text{Na}_8\text{Si}_{46}$. The top of the framework valence band defines the zero of energy. The remnant of what remains of the semiconducting gap in Na free Si clathrate is the gap from 0.00 to ~ 0.75 eV. The conduction band begins near 0.75 eV, and the Fermi level is shown as a vertical dashed line at 1.35 eV.

largest Knight shift, as is observed (Fig. 2). The magnitudes of the s DOS for the other two sites are comparable, with a slightly larger contribution from $16i$ sites which should have a larger Knight shift than $6c$ sites. This is reversed compared with the experimental result. However, the s DOS varies rapidly on a small energy scale and the relative shifts of the $16i$ and $6c$ sites are sensitive to small changes in the position of the Fermi level. The shift for the $24k$ site will, however, always remain much larger than for the other two.

Although the $\text{Na}_8\text{Si}_{46}$ clathrate sample is metallic, it has not been found to be superconducting above 4 K.¹³ Superconductivity with T_c in the 4–6 K range has been reported in $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ and in other members of the $\text{Na}_x\text{Ba}_6\text{Si}_{46}$ series.^{2,14} Shimizu *et al.*¹⁵ studied the ^{29}Si spectrum of $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ in a static NMR experiment and reported three broad (~ 300 ppm) bands that they assigned to $16i$, $6c$, and $24k$ Si sites based on their relative intensities, as we have done here. The peaks assigned to $6c$ and $24k$ sites were not well resolved, especially at room temperature. Korringa-type relaxation was observed for all three peaks, confirming the metallic nature of this sample. The NMR shifts reported for the $6c$ and $24k$ sites are similar to those found here for $\text{Na}_8\text{Si}_{46}$; however, that for the $16i$ site is much larger, by an additional ~ 1000 ppm.

In their theoretical study of Ba-doped Si_{46} , Saito and Oshiyama¹⁶ reported that the conduction-band states are very much altered from undoped Si_{46} , indicating considerable hybridization between the Si framework conduction states and Ba states. For the Na-doped Si_{46} studied here, we find a very different situation. The first few conduction bands of $\text{Na}_8\text{Si}_{46}$ are nearly identical with the conduction bands of the metal-free Si_{46} framework, but are simply brought closer in energy to the framework valence bands by ~ 0.5 eV, consistent with a “rigid-band model.” In our calculated total electronic DOS for $\text{Na}_8\text{Si}_{46}$, the top of the framework valence band is at 0 eV, and the dashed line indicates the position of the Fermi level (1.35 eV) in the conduction band produced by the extra eight electrons contributed by the eight Na atoms.

Saito and Oshiyama¹⁶ noted that the silicon Fermi-level DOS in $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ was about twice (47.9 states/eV) that expected from simply filling the 14 electrons from 6 Ba (12 electrons) and 2 Na (2 electrons) per unit cell into the conduction band of metal-free Si_{46} . In order to account for this, they proposed that hybridization with the metal orbitals (primarily the Ba $5d$ orbitals) resulted in a sharply peaked den-

sity of states close to the Fermi level. This would explain the high DOS at the Fermi level and why superconductivity is observed in Ba-containing Si_{46} compounds, but not in $\text{Na}_8\text{Si}_{46}$. Shimizu *et al.*¹⁵ used this observation to interpret their ^{29}Si NMR result. Based on the measured T_1 relaxation times, which increased in the order $24k > 6c > 16i$, they concluded that the ^{29}Si NMR relaxation is dominated by the Fermi contact term, and suggested that the $6c$ and $16i$ sites in $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ are more strongly hybridized by guest atom orbitals, particularly Ba $5d$ states, than are the $24k$ sites. The $16i$ sites as identified by Shimizu *et al.* are significantly shifted (by ~ 1000 ppm) between $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_2\text{Ba}_6\text{Si}_{46}$. This shift is not simply explained by a change in the s -state DOS for these sites because the $5d$ orbitals from barium do not contribute directly to the NMR shift of ^{29}Si . However, the presence of barium with additional electrons donated to the conduction band will considerably alter χ_s^e in Eq. (1).

In conclusion, the solid-state MAS NMR spectrum of $\text{Na}_8\text{Si}_{46}$ clathrate clearly shows the three resonances expected for the inequivalent Si sites in this compound. The large positive Knight shifts observed for these lines demonstrates the metallic nature of the sample. The integrated area under each peak, taking account of contributions from spinning side bands, shows the ratio of the three sites to be $[15.7 \pm 0.3]:[6.5 \pm 0.6]:[23.8 \pm 0.5]$ compared with the 16:6:24 ratio expected for the ideal stoichiometry. This result is supported by the site occupancies obtained from Rietveld analysis of x-ray powder-diffraction data, and clearly shows that the compound is best formulated as a semimetallic clathrate rather than as an ionic Zintl phase with defects in the tetrahedral framework (i.e., $\text{Na}_8\text{Si}_{44}\square_2$). Our LDA calculations indicate that there is a much greater s -state DOS at the $24k$ site compared with the $6c$ and $16i$ sites, consistent with the observed ^{29}Si Knight shifts. The NMR spectrum then provides a detailed and useful probe of the local DOS at Fermi level, which also determines the observed superconductivity^{2,14–16} and the thermopower characteristics³ in these tetratelluride clathrates.

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- ¹⁷X-ray-diffraction analysis showed only trace (<5% w/w) contamination by $\text{Na}_x\text{Si}_{136}$. Subsequent ^{29}Si NMR on pure $\text{Na}_x\text{Si}_{136}$ samples with varying ($x=4\text{--}23$) compositions did not show evidence for the impurity peak at ~ 590 ppm.