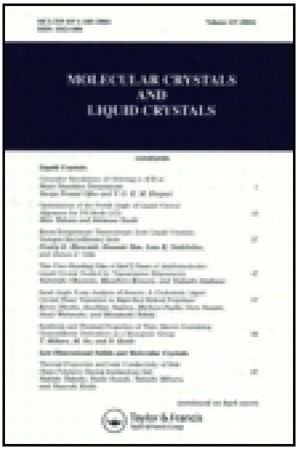

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

NMR Studies of Silicon Clathrate Compounds

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Version of record first published: 27 Oct 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 497-502
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NMR Studies of Silicon Clathrate Compounds

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NMR spectra of ^{29}Si and ^{137}Ba in silicon clathrate compounds, $Na_xBa_ySi_{46}$, Na_xSi_{136} and $Ba_8T_xSi_{46}$ (where T = Au, Ag, and Cu) are reported. We found that the local density of states at the Fermi level increases with rising superconducting transition temperature. The silicon S1 site was suggested to hybridize with Ba-orbital in the superconducting clathrate and has a large local density of states.

Keywords: NMR; silicon clathrate compounds; superconductivity

INTRODUCTION

Silicon clathrate compound, $Na_xBa_ySi_{46}$ and Na_xSi_{136}, is one of the most important classes in various silicon network systems. The structures are given by filling in space with silicon polyhedra (Si_{20}, Si_{24}, and Si_{28}) which can contain alkali-metals and / or Ba atoms inside, as illustrated in Fig. 1 for Si_{46} compound[1-3]. Band calculations[4,5] made an interesting prediction that the hypothetical undoped Si_{46} is a semiconductor with a band gap wider by ~0.7eV than that of diamond structure Si. Thus, the synthesis of pure Si_{46} crystal is an important target in semiconductor technology. Another important feature is occurrence of superconductivity in Si_{46} clathrate[3]. Because of the structural similarities[1] and differences, compared

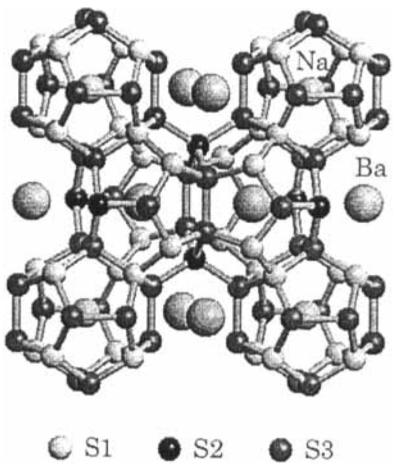

FIGURE 1 Structure of $Na_2Ba_6Si_{46}$. The large sphere are Ba atoms occupying the center of Si_{24} polyhedra, and the smaller sphere located at the center of Si_{20} polyhedra are Na atoms. There are three kinds of inequivalent Si site: S1, S2, and S3. The S2 silicon is connecting two neighboring Si_{20} cages. The S2 and S3 sites are belonging to both Si_{20} and Si_{24} polyhedra. In Ba_8Si_{46}, Na atoms are replaced by Ba atoms. In $Ba_8T_6Si_{40}$ (where T = Cu, Ag, and Au), the S2 silicons are replaced by T-atoms. In Na_xSi_{136}, the building blocks are Si_{20} and Si_{28} polyhedra.

with fullerene networks such as A_3C_{60} and $A_3Ba_3C_{60}$ superconductors (where A = alkali metal), the studies of the electronic structure and superconducting mechanism in Si_{46} system would lead to a deeper common understanding in electronic states and superconducting mechanism of covalent network system. In this point of view, we are investigating systematically the electronic states both in Si and fullerene networks. Here, we present NMR results on silicon clathrate compounds.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The samples studied are summarized in Table I. The crystal structure of $Ba_8T_6Si_{40}$ (where T = Cu, Ag, and Au) is obtained by replacing the S2-silicons

TABLE I. Samples studied and superconducting (SC) transition temperature, T_c. The composition of $Ba_8T_6Si_{40}$ (T = Cu, Ag, and Au) is nominal.

Sample	T_c (K)
Ba_8Si_{46}	8.0
$Na_{0.2}Ba_{5.6}Si_{46}$	4.2
$Na_{2.9}Ba_{4.6}Si_{46}$	3.5
Na_4Si_{136}	non-SC (examined down to 2K)
$Na_{19}Si_{136}$	non-SC (examined down to 0.15K)
$Ba_8Cu_6Si_{40}$	non-SC (examined down to 0.15K)
$Ba_8Ag_6Si_{40}$	non-SC (examined down to 0.15K)
$Ba_8Au_6Si_{40}$	non-SC (examined down to 2K)

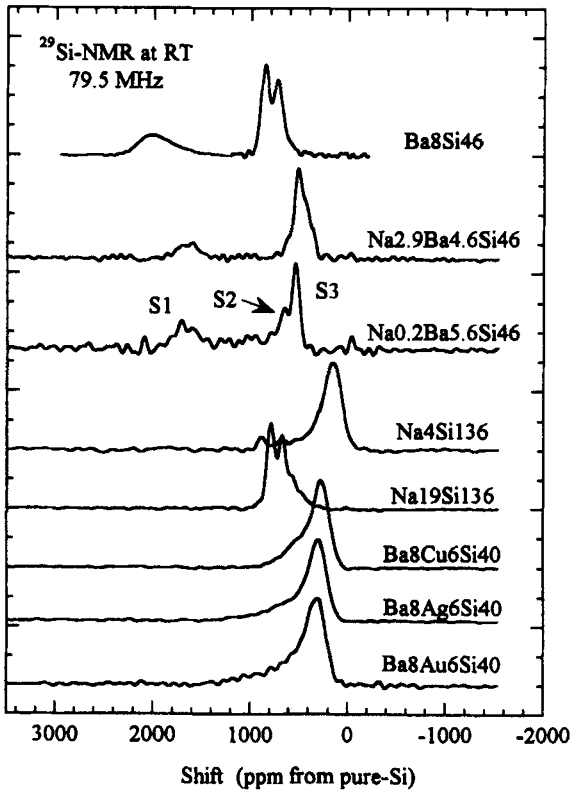

FIGURE 2. ^{29}Si NMR spectra of silicon clathrate compounds listed in Table I. The intensity ratio is not correct.

by *T*-atoms from the Si_{46} structure. Superconductivity is observed only in Si_{46} compounds containing Ba atoms. The ^{29}Si-NMR and ^{137}Ba-NMR spectra were taken using conventional pulse NMR technique at a magnetic field of 9.4 T. The experimental details have been described in a previous paper[6]. Figure 2 shows the ^{29}Si-NMR spectra at room temperature (RT). The NMR frequency shift was measured from that of a semiconducting silicon powder. The shift is sum of orbital shift (chemical shift) and Knight shift, K. It is important to note that the Knight shift is proportional to spin susceptibility at each atomic site and almost temperature (T)-independent in the case of metal. Therefore, Knight shift in metal is given by

$$K \sim \chi_P \sim n(E_F),$$

where $n(E_F)$ and χ_P are the electronic density of states at the Fermi level and Pauli spin susceptibility, respectively[7].

In the previous NMR studies[6,8], the orbital shift (where $K = 0$) was estimated to be −300ppm from the pure silicon for Si_{46} compounds and $Na_{19}Si_{136}$. If this value is applied to the present data, the ^{29}Si-NMR spectra suggest that all the materials studied here are metallic at each silicon site. We also notice that the superconducting compounds show a S1 signal with a large Knight shift (~2000 ppm), along with S2 and S3 signals with the smaller Knight shift of ~900 ppm. The site assignment to the inequivalent silicon atoms is found from Figures 1 and 2. The center of gravity of ^{29}Si Knight shift of nonsuperconductiong $Na_{19}Si_{139}$, which is 1029 ppm at 4.2K, is comparable to those of superconducting Si_{46} compounds, for example 1248 ppm at 4.2K in $Na_{2.9}Ba_{4.6}Si_{46}$[8].

Figure 3 shows ^{137}Ba-NMR spectra at 4.2K where the shift was measured from $Ba(NO_3)_2$ solution (1M) at RT. The ^{137}Ba Knight shift, given by shift from that of $Ba(NO_3)_2$ solution, is found to increase with rising T_c.

From these spectra, we know that the T_c rises with increasing $n(E_F)$ at Ba site (and silicon site). Furthermore, an importance of S1 site having large density of states is suggested for the occurrence of superconductivity. The band calculation by Saito & Oshiyama showed that the large density of states at the Fermi level[4] responsible for the superconductivity results from the hybridization between Ba *d*-orbital and silicon orbitals. In this connection, we speculate the S1 site strongly hybridizes with Ba-orbital. Because Ba atoms mainly occupy centers of Si_{24} cages in an ideal stoichiometry sample, $Na_2Ba_6Si_{46}$, a phonon mode responsible for the superconductivity would be a kind of "breathing mode" of Si_{24} cages.

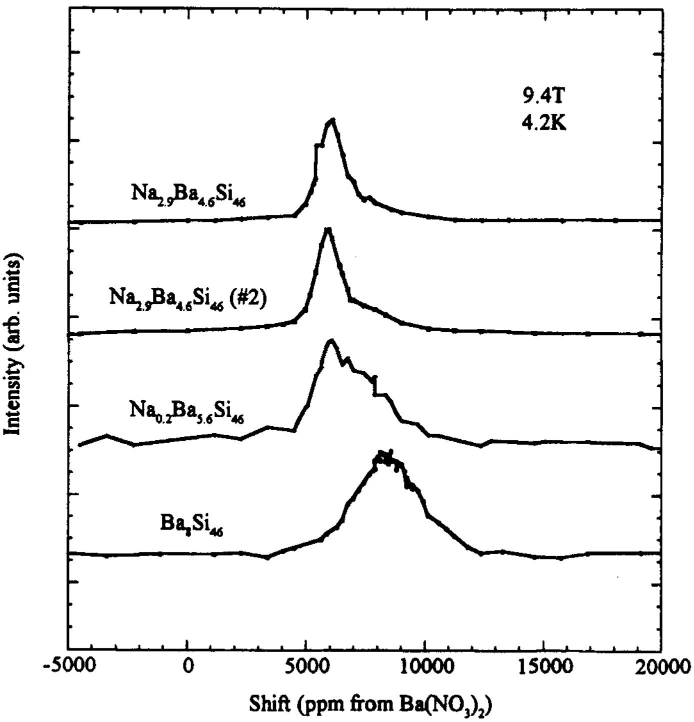

FIGURE 3 ^{137}Ba-NMR in silicon clathrate compounds listed in Table I. The NMR spectra of $Ba_8T_6Si_{40}$ are not included, because the spectra are very broad (more than 4.5×10^4 ppm (~2MHz)), probably due to a large quadrupole interaction.

Acknowledgments

This work was supported in part by the Grant-in Aid for Scientific Research on the Priority Area "Fullerenes and Nanotubes" by the Ministry of Education, Science and Culture of Japan.

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