Vibrational modes in silicon clathrate compounds: A key to understanding superconductivity


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(Received 29 March 2002; published 19 July 2002)

Several doped type-I silicon clathrates (Na8@Si46, K8@Si46, Ba8@Si46 and I8@Si46) have been investigated both experimentally by inelastic neutron scattering and x-ray-absorption spectroscopy and theoretically by ab initio calculations. We find that Ba atoms have a stronger coupling with the host lattice than Na or K ones. We show that in the superconductor Ba8@Si46 the coupling is effectively done by host acoustic phonons exciting guest acoustic modes. These features suggest that the host-guest vibrational coupling is a crucial parameter to explain the appearance of superconductivity in addition to the density of states near the Fermi level.

DOI: 10.1103/PhysRevB.66.014532 PACS number: 74.70.Wz, 61.10.Ht, 63.20.Kr, 78.70.Nx

I. INTRODUCTION

Type-I clathrates have a cage-type structure obtained by a face-shared assemblage of silicon polyhedra that form around guest atoms during the synthesis.1 Column-IV (Si, Ge, Sn, and hypothetical C) clathrates are attracting much attention because of their superconducting2–6 wide-gap,7,8 thermoelectric,7,8 or ultrahard9,10 properties. The type-I silicon clathrate lattice is an arrangement of two pentagonal dodecahedra (Si20) and six tetrakaidecahedra (Si24) offering eight sites per unit cell for guest alkali, alkaline-earth or halogen atoms (M).11 The resulting formula is therefore (M@Si20)2(M@Si24)6Si48 or for the sake of simplification M8@Si48. In particular, endohedrally Ba-doped silicon clathrates of the type I constitute the only known sp3 silicon based material superconductor at normal pressure. In fact, superconductivity has been reported for Ba8@Si46,12 Na8Ba4–x@Si46,2 Ba8@[Ga16Ge30],13 and Ba8@[TMxSi46–x] (TM = Au, Ag, Cu)(Ref. 14) clathrates with a maximum Tc of 8 K for Ba8@Si46. Their superconductivity mechanism is still disputed. Some authors propose a phonon-mediated Bardeen-Cooper-Schrieffer (BCS) mechanism as observed in doped fullerences.15 According to this, Tc depends on two terms, the density of states (DOS) at the Fermi level N(EF) and the electron-phonon coupling factor. Recent measurements16 show that Ba8@Si46 has a type-II superconductivity behavior, while Na8@Si46 has no superconductivity. Some theoretical predictions give a higher N(EF) in Ba8@Si46 than in Na8@Si46.17 This is understood as an hybridization effect: Ba8d orbitals are more hybridized with silicon than Na8d states.5,17 Nevertheless, this results raise the problem of the total absence of superconductivity in Na8@Si46 for which N(EF) ≠ 0.18 This paper reports insight in the understanding of the parameters that govern the superconductivity in such materials, especially the coupling between the guest atom and the host lattice. For this purpose, we characterize the coupling modes between a guest atom (Na, K, Ba, and I) and the silicon host (Si20 or Si24 cage) both by inelastic neutron scattering, extended x-ray-absorption fine structure (EXAFS) spectroscopy and ab initio calculations. We experimentally show the increase of the hybridization inside the series Na, K, Ba, and I guest atoms. We also find a correlation between the disappearance of the guest atom localized mode and the appearance of the superconductivity. All the experiments are in good agreement with our calculations on these systems.

II. EXPERIMENTAL PROCEDURE

Different means have been used for the elaboration of each sample. Na8@Si46 was prepared by thermal decomposition of the Zintl phase NaNi under argon flow at 680 K,19 K8@Si46 was obtained by pyrolysis of KSi under secondary vacuum.20 For Ba8@Si46 and I8@Si46,13 high-pressure high-temperature (HPHT) conditions are required.12,11 The inelastic neutron-scattering experiments were carried out at the Institut Laue Langevin in Grenoble on the IN6 beam line, equipped with a time-of-flight spectrometer. The incident wavelength was 4.12 Å and the momentum transfer ranged between 0.39 and 2.56 Å−1. The incident neutron beam, extracted by a triple monochromator crystal assembly, was time focused by a Fermi chopper. The time-of-flight path was 248 cm in length with an angle range from 10° up to 114°. The detection was performed using 337 elliptical 3He detectors. Some corrections were applied on the obtained spectra in order to take into account the background and aluminum cell contributions. An integration over the full angular range resulted in obtaining an incoherent approximation of a phonon DOS.21 All the samples are fine powders (about 300 mesh), pressed between two aluminum foils. For the superconductor Ba8Si46, EXAFS was performed at the BM29 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a Si (111) helium cooled...
double crystal monochromator working at 50% detuning for harmonic reduction. Samples were placed in a He DISPLEX cryostat and transmission spectra at the Ba K edge were recorded at three different temperatures, namely 20, 100, and 300 K. Three different scans were recorded at each temperature and then averaged. Measurements at low temperature are essential for the correct interpretation of the spectra since the Ba-Si and Ba-Ba coupling factors are weak leading to a large thermal damping of the signal.

III. RESULTS

A. Inelastic neutron scattering

Inelastic neutron scattering can provide a quantitative measure of the phonon density of states (PDOS) of a solid as a function of energy. In general to obtain the PDOS from inelastic neutron-scattering data in a multielement solid needs the introduction of a detailed model of the lattice dynamics. Nevertheless, quantitative information can be extracted if, for instance, the different atomic species participate in totally decoupled vibrational modes. In Fig. 1 are depicted the inelastic-scattering data determined at 300 K for various silicon clathrates (a)–(e) and pure silicon (f). α and β design the low-frequency molecular modes (mmf) corresponding to the rattling of the entrapped atoms in the cages. AM, OM, and (A + O)M stand, respectively, for acoustic modes, optic ones, and the mixed contribution of the two.

FIG. 1. Inelastic-scattering data determined at 300 K of various silicon clathrates (a)–(e) and pure silicon (f). α and β design the low-frequency molecular modes (mmf) corresponding to the rattling of the entrapped atoms in the cages. AM, OM, and (A + O)M stand, respectively, for acoustic modes, optic ones, and the mixed contribution of the two.

For a given position of the Ba atom in the cages, we can compute single- and multiple-scattering paths contributing to the EXAFS signal and adjust some fitting parameters using the FEFFIT code.24 Figure 2 displays the EXAFS of Ba$_4$Si$_{46}$ at the Ba K-edge at $T = 20$, 100, and 300 K. The Fourier transform of the experimental EXAFS signal is shown in Fig. 3. EXAFS oscillations were expressed in terms of the photoelectron wave number $k = 1/\hbar \sqrt{2m(E - E_0)}$ where $m$ is the electron mass and $E_0$ is chosen at the inflexion point of the threshold and further adjusted in the fitting procedure.

For a given position of the Ba atom in the cages, we can compute single- and multiple-scattering paths contributing to the EXAFS signal and adjust some fitting parameters using the FEFFIT code.24 In this formalism the total EXAFS signal $\chi(k)$ writes

$$\chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k),$$

where $\chi_{\Gamma}(k)$ is the contribution to the signal of each considered single- or multiple-scattering path $\Gamma$. This contribution is evaluated as

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TABLE I. Si modes, guest atom molecular modes frequencies (mmf’s), and $K$ factor coupling in the harmonic oscillator framework. Calculations have been performed considering the displacement of the guest atoms towards the center of a pentagon (cp) or an hexagon (ch) or towards the atom of a pentagon (ap) or an hexagon (ah).

<table>
<thead>
<tr>
<th></th>
<th>$Na_{8} Si_{46}$</th>
<th>$K_{8} Si_{46}$</th>
<th>$Ba_{8} Si_{46}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmf (neutrons) in $Si_{20}$</td>
<td>$18 \pm 1$</td>
<td>$20.0 \pm 0.5$</td>
<td>$14.4 \pm 0.5$</td>
</tr>
<tr>
<td>mmf (x-ray diffraction) in $Si_{20}$</td>
<td>$23$</td>
<td>$12.7$</td>
<td></td>
</tr>
<tr>
<td>mmf (calculated) in $Si_{20}$ (cp)</td>
<td>$18.8$</td>
<td>$14.6$</td>
<td></td>
</tr>
<tr>
<td>mmf (neutrons) in $Si_{24}$</td>
<td>$10.3 \pm 0.2$</td>
<td>$12.2 \pm 0.2$</td>
<td>$7.8 \pm 0.2$</td>
</tr>
<tr>
<td>mmf (x-ray diffraction) in $Si_{24}$</td>
<td>$15.9$</td>
<td>$8.0$</td>
<td></td>
</tr>
<tr>
<td>mmf (calculated) in $Si_{24}$ (ap,ah,cp,ch)</td>
<td>$8.4, 9.6, 10.3, 12.9$</td>
<td>$8.6, 9.2, 8.9, 10.6$</td>
<td></td>
</tr>
</tbody>
</table>

$K_{exp}$ in $Si_{20}$ (neutrons) | $1.8 \pm 0.2$ | $3.8 \pm 0.2$ | $7.0 \pm 0.5$ |

$K_{ch}$ in $Si_{20}$ (cp) | $1.8$ | $7.1$ |

$K'_{ch}$ in $Si_{20}$ (cp) | $1.32$ | $3.68$ |

$K_{exp}$ in $Si_{24}$ (neutrons) | $0.60 \pm 0.03$ | $1.48 \pm 0.05$ | $2.1 \pm 0.1$ |

$K_{ch}$ in $Si_{24}$ (ap,ah,cp,ch) | $0.40, 0.52, 0.6, 0.94$ | $2.50, 2.88, 2.9, 3.8$ |

$K'_{ch}$ in $Si_{24}$ (ap,ah,cp,ch) | $0.4, 1.16, 0.64, 0.36$ | $1.24, 3.68, 2.4, 1.68$ |

$a$ mmf in meV.

$^b$ From Ref. 37.

$^c$ From Ref. 29.

$^d$ $K$ in eV/Å$^2$

$^e$ $K'$ in eV/Å$^4$

\[
\chi(k) = \text{Im} \left[ \frac{N_1 S_0^2 F_1(k)}{2kR^2_1} e^{i[2kR_1 + \Phi_1(k)]} e^{-2k^2 \sigma^2_1} \right],
\]

where $N_1$ is the degeneracy of the path, $S_0^2$ is the passive electron reduction factor, $R_1$ is the length of the path, and $\sigma^2_1$ is the root-mean-square displacement of the path length. The effective backscattering amplitude $F_1(k)$ and phase shift $\Phi_1(k)$ are computed by FEFF.

We consider all the photoelectron scattering paths having as origin the barium atoms and with a maximum half scattering length of 7 Å. Depending on the considered position of the Ba atom inside the $Si_{24}$ and $Si_{20}$ cages, up to 100 different scattering paths had to be considered. We have checked that the number of pathways is significant enough so that the truncation of the sum in Eq. (1) has converged to the real EXAFS signal.

In a previous work,\textsuperscript{27} we showed that the equilibrium position of the sodium atoms is out of the center of the $Si_{28}$ cage in a type-II silicon clathrate. The displacement, that can be viewed as a strong Jahn-Teller effect, was about 1 Å indicating a weak coupling. Such behavior has been also theoretically predicted in alloyed germanium clathrates,\textsuperscript{28} even though no data are yet reported for $Si_{24}$ cages.

The signal between 2 and 4 Å in Fig. 3 corresponds to the contribution of single-scattering paths involving the barium atom and the silicon ones of the $Si_{20}$ and the $Si_{24}$ cages. We have first fitted the corresponding filtered signal using as

![Graph](image_url)

FIG. 2. Dots: Experimental EXAFS oscillations of $Ba_{8} Si_{46}$ at the Ba $K$-edge at $T=20$, 100, and 300 K. The signal has been multiplied by $k^3$. Lines: corresponding fit of the data obtained with the Ba atoms placed at the center of the cages (see text for details). We note that at 300 K, the noise level dominates the signal for $k$ values higher than 10 Å$^{-1}$.
model structure the one obtained by x-ray diffraction but allowing the out of center displacement of the barium atom. Our best fit was obtained considering Ba atoms at the center of both the Si_{20} and Si_{24} cages. This fit allows as well to correct the phase-shift origin given by the FEFF code for Ba-Si paths. We find a correction of -1.5 eV that we used in the following analysis. We have then simultaneously fitted the EXAFS signal of the three spectra at 20, 100, and 300 K, considering the Einstein model for the dynamics of the interatomic distance, with a different Einstein temperature $u$ for the average Si-Ba single-scattering path for each type of cage. The fits shown in Figs. 2(a)–2(c) give $\theta_B^{20}_{Ba-Si} = 350 \pm 100$ K and $\theta_B^{24}_{Ba-Si} = 260 \pm 40$ K with associated energies of $E_B^{20}_{Ba-Si} = 30 \pm 9$ meV and $E_B^{24}_{Ba-Si} = 22 \pm 4$ meV.

The total experimental EXAFS signal at 20 K between 4 and 14 Å$^{-1}$ was then fitted. The result is shown in panel (a) of Fig. 4. Here we have considered a total of 44 scattering paths. The different contributions to the total signal are shown in panels (b)–(e) of Fig. 4. We observe that the addition of the signals produces a strong “beating” at about 9.5 Å$^{-1}$ in excellent agreement with the experiment as shown in Fig. 4(a). Phase shifts between the different components contributing to the EXAFS signal appear by displacing one of the Ba atoms, and immediately shift the beating position or give rise to its disappearance. We claim that barium occupy exactly the center of the cages at low temperature. We note also the importance of the Ba-Ba scattering paths at high k where its amplitude is comparable to the total multiple-scattering signal. In our EXAFS model, the only fitted parameters were the harmonic thermal characteristic of Ba-Ba scattering paths, the corresponding shift of $E_0$ (that was found to be zero), and an associated thermal term for the multiple-scattering paths. The Einstein temperature associated to the Ba-Ba correlations is of $\theta_{Ba-Ba} = 90 \pm 50$ K, or its associated energy, $E_{Ba-Ba} = 8 \pm 5$ meV. The sensitivity of EXAFS to the factors affecting the amplitude of the $\chi(k)$ oscillations is much smaller than those affecting the phase of the signal. This explains the lower accuracy of the EXAFS mmf values when compared to neutrons.

C. Ab initio calculations

There are few ab initio calculations on the lattice vibrations of silicon clathrates. Our ab initio calculations were performed within the local-density approximation. We adopt a pseudopotential approach and a numerical-atomic-orbitals (NAO) expansion of the wave functions using the SIESTA code. We calculated the potential energy curves of guests by displacing a single guest atom (Na, Ba) in one of the cages (Si_{20} or Si_{24}) while keeping all other guest atoms fixed.

For Si_{20} we have computed the energy curve when the guest atoms (Na, Ba) are displaced towards the center of one pentagon or towards a silicon atom. For Si_{24} we have computed the energy curves with four configurations corresponding to displacements toward (i) the center of an hexagon or (ii) a pentagon or towards (iii) an atom of an hexagon or (iv) an atom shared only by pentagons. The fitting parameters of guest-framework interaction energy potentials is written as $E(x) = \frac{1}{2} Kx^2 + \frac{1}{4} K'x^4$. All the results are summarized in Table I together with the experimental data.

Our calculations show that there exist an anisotropy of rattling of the guest atoms inside the Si_{24} cages, characterized by vibrations that are softer in the direction of the atoms of the cage and harder when moving towards the center of the polyhedra. If we can quantify the degree of calculated anisotropy as the maximum of the difference between the different projections of the atomic movement, it appears that the anisotropy for the Ba atom is about 20%, half the one of Na atoms.

IV. DISCUSSION AND CONCLUSION

The comparison between the calculated and experimental values of the guest molecular modes frequencies (mmf)
shown in Table I should take into account the anisotropy of the guest atom movement evidenced by our calculations. The inelastic neutron-scattering as well as the x-ray-diffraction data\textsuperscript{20,37} correspond to the time averaged value of the calculated mmf in the different directions.

The EXAFS atomic displacement parameters obtained for a single-scattering path between atoms X and Y, \( \sigma_{X-Y}^2 \), is to be related with the corresponding atomic displacements \( u_X \) and \( u_Y \):

\[
\sigma_{X-Y}^2 = \left\langle (u_X - u_Y)^2 \right\rangle = \left\langle u_X^2 \right\rangle + \left\langle u_Y^2 \right\rangle - 2 \left\langle u_X u_Y \right\rangle \\
\quad = \left\langle u_X^2 \right\rangle + \left\langle u_Y^2 \right\rangle - 2 \sqrt{\left\langle u_X^2 \right\rangle \left\langle u_Y^2 \right\rangle} \Phi.
\]

Here \( \Phi \) is a parameter measuring the degree of correlation between the displacements of X and Y atoms. \( \Phi \) will be zero for totally decorrelated pairs of atoms, \( \Phi = 1 \) in the case of acoustic coupling, and \( \Phi = -1 \) for optical coupling.

The EXAFS value when considering the Ba-Ba scattering paths corresponds to an average of the mmf in the direction of the faces of the polyhedra (the direction of the Ba-Ba neighbors). On the other side when considering EXAFS single-scattering Ba-Si paths inside the cages we shall take into consideration the directions towards the silicon atoms.

For the weakly coupled Na atom, neutron and calculations agree remarkably well when considering the displacement towards the center of the pentagons, both in the Si\textsubscript{36} and Si\textsubscript{40} cage. In the Si\textsubscript{40} cages of Na\textsubscript{8} @ Si\textsubscript{46}, the calculated average mmf gives also a value of 10.3 eV (the same as that in the direction of the pentagons). The mmf projection in the Na-Si direction is about 20% smaller than the average value given by the neutron or the x-ray-diffraction experiments.

For Ba\textsubscript{8} @ Si\textsubscript{46}, neutron and x-ray-diffraction data agree remarkably well. On the contrary, the calculated mmf seems to slightly overestimate the result from the neutron inelastic-scattering experiment. This could be a signature of a stronger coupling but can also be associated with defects in the Ba pseudopotential. Nevertheless, as already discussed, calculations show that the anisotropy in the thermal displacement of the Ba atom is half the one for the Na case. Consequently, we should consider a reduction of 10% of the average values of neutron or diffraction experiments to obtain the projection in the direction of silicon atoms and confront this values with the EXAFS ones through Eq. (3). As we do not know how silicon displacements are projected, in order to obtain an estimate of \( \Phi \), we will consider directly the values of neutron and diffraction experiments and add an additional 20% in the error estimation. Remarkably enough, the obtained coupling constants summarizing those calculations are the same for Ba-Si in both type of cages: \( \Phi_{Ba-Si,36}^{Ba-Si} = \Phi_{Ba-Si,19}^{Ba-Si} = -0.35 \pm 0.1 \).

Let us now consider the Ba-Ba scattering paths. More than 90% of the Ba-Ba next-nearest neighbors in the Ba@Si\textsubscript{46} structure are between Ba atoms in the Si\textsubscript{36} and Ba atoms in the Si\textsubscript{40} cages. The corresponding EXAFS signal contribution should then be mainly characterized by the average of both cages mmf in the direction of the center of the polyhedra. As we have seen for the Na case, the mmf signal towards the center of the pentagons can be considered as representative of the average mmf. We can then directly consider the x-ray-diffraction or neutron values without modification and use Eq. (3) that gives \( \Phi_{Ba-Ba} = 0.4 \pm 0.2 \).

It is remarkable that the absolute value of the three coupling constants are equivalent, and that the sign of \( \Phi_{Ba-Ba} \) is opposed to the one of the Ba-Si. We conclude that the Ba atoms are acoustically coupled between them through optical Ba-Si coupling. This corresponds to the coupling of host acoustic modes with guest acoustic excitations.

The energy of the molecular mode frequencies (mmf’s) will depend on the mass of the guest, and on the overlapping between electron valence shell of the guest atom and the Si\textsubscript{36-3p} electrons. This last term will be a function of the ratio of the cage, the guest atom radius, and on the energy difference of the atomic energy levels. Assuming a classical harmonic oscillator, one easily observes that the coupling factor \( K_{exp} \) increases in the series Na, K, to Ba. This is also correlated to the softness of the Si stretching modes, clearly showing that the hybridization becomes more and more efficient from Na to Ba. The softening of the Si modes coincides with the electron transfer in the conduction band. This is due to the increase of the electron clouding between Si atoms. The introduction of metallic atoms in the host network (Ba\textsubscript{8} @ Ag\textsubscript{6}Si\textsubscript{40}) has clearly the effect of reducing the host-guest coupling.

The origin of the hybridization remains complex. For example, the extension of the Slater orbital for the guest atom plays an important role but do not explain entirely the coupling strength. We notice that the ionic radius is 0.95 Å in sodium and about 1.34 Å for potassium and barium while barium is more coupled than potassium (see below). For iodine, we found an acceptor state.\textsuperscript{38} Iodine radii ranges between the neutral radius (1.4 Å) and the Pauling ionic radius 2.16 Å (in \( \Gamma^- \) state): this is the more coupled system. Nevertheless, a more efficient hybridization alone does not explain the superconductivity. As mentioned above the difference in ionization potentials between the guest and the host atom is a crucial parameter. Soft x-ray emission spectroscopy has been applied in order to visualize the electronic density of states at the Fermi level.\textsuperscript{39} The experimental e-DOS showed a sharp peak at \( E_F \) for both the nonsuperconductor Na\textsubscript{8} @ Si\textsubscript{46} and superconductor Ba\textsubscript{8} @ Si\textsubscript{46}.

In order to study the second term in the BCS theory, i.e., the electron-phonon coupling, it is of high importance to notice that the lowest energy molecular mode has been predicted by Yoshizawa et al.\textsuperscript{40} This group argues that the Jahn-Teller distortion correlated with the superconductivity is due to the low-frequency phonon close to 12 meV in Si\textsubscript{36}, this polyhedra having the strongest vibronic coupling constant. We actually observe this low-frequency phonon and it is therefore of high interest to compare its energy with the superconducting properties of each of the samples. All the mmf’s range around 12 meV (see Table I). An efficient electron coupling involves a strong coupling between the guest atom vibration mode and the silicon cage. As a consequence, with an increasing coupling, the mmf must progressively broaden, to finally disappear in the phonon density of states, i.e., the amplitude of the mmf is inversely proportional to the K coupling factor. We observe in Fig. 1 that the mmf modes...
AFS shows that the Ba atom in Ba$_8@$Si$_{46}$ is well localized in Na guest has been theoretically predicted at low atom. Our neutron inelastic-scattering data and calculations corresponding to Si$_{20}$ cages have a weak intensity independently of the nature of the guest atom. The electron-phonon coupling can be efficient in such cages. However, the mmf corresponding to Si$_{24}$ cages has a high intensity in sodium atom and decreases strongly in barium (potassium being an intermediate case) inspite of the higher coherent neutron-scattering factor of Ba. We also observe in Table II that the FWHM of the Ba mmf in the Si$_{24}$ cages is almost two times the one of Na or K. Therefore sodium or potassium are weakly coupled to the Si$_{24}$ cage while barium atoms show a much stronger coupling. This could be correlated to the occurrence of the superconductivity in Ba$_8@$Si$_{46}$. In fact, EXAFS shows that the Ba atom in Ba$_8@$Si$_{46}$ is well localized in the cage center and phonon-coupled to the silicon network. Contrarily, in Na$_8@$Si$_{46}$ a strong anharmonicity due to the Na guest has been theoretically predicted at low temperatures and is associated with the rattling of the guest atom. Our neutron inelastic-scattering data and calculations (that as shown in Table I give an average $k^1/k$ that is bigger in the Na that in the Ba case) are compatible with such prediction. This type of anharmonicity will not be favorable to the dynamic guest-host coupling necessary for the superconducting behavior.

We observe the highest coupling in the iodine case since no mmf is observed. Unfortunately, the strong expected electron-phonon coupling is counterbalanced by a zero density at the Fermi level: the iodine level is not a superconductor. We note here that in recent ab initio calculations it was reported a density of states with a Fermi level of I$_8@$Si$_{46}$ located just beneath the top of the valence band. Nevertheless, this prediction does not correspond to the real stoichiometry of the iodine intercalated clathrate that is more complex (see the introduction) and conductivity measurements report an insulating state. We can then expect that the Fermi level just coincides with the top of the valence band. The case of Ba$_6@Ag_6Si_{40}$ is more difficult to discuss due to the lack of data on the electronic density of states.

In conclusion, we have reported the experimental evidence of the coupling between the guest atom and the cage host through host acoustic modes. Such coupling was deduced from both the phonon DOS and the vibrational motion measured by inelastic neutron-scattering and EXAFS spectroscopy. We found that the main parameters to be correlated to the superconductor properties are the host-guest vibrational coupling inside the Si$_{24}$ cage and the density of states at the Fermi level. Coupling inside the Si$_{24}$ cages is essential to obtain the acoustic excitation of the Ba subnetwork. It appears that the enhancement of the critical temperature needs a large atomic radius of the donor atom in the Si$_{24}$ cage while no such condition is required for donor atoms located in Si$_{20}$ cages where the coupling is already strong.

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PHYSICAL REVIEW B 66, 014532 (2002)