Electronic structure and superconducting gap of silicon clathrate Ba$_8$Si$_{46}$ studied with ultrahigh-resolution photoemission spectroscopy


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We study the electronic structure and superconducting transition of silicon clathrate Ba$_8$Si$_{46}$ (\(T_c = 8\) K) using photoemission spectroscopy. We observe a narrow band at the Fermi level (\(E_F\)), whose width (~0.3 eV) is substantially smaller than that of band structure calculations (~1.5 eV). Ultrahigh-resolution measurements show a superconducting gap at 5.4 K [2\(\Delta(0)/k_BT_c = 3.51\)]. Fine structures associated with phonons are observed within 70 meV of \(E_F\). These results characterize Ba$_8$Si$_{46}$ as a weak-coupling superconductor most probably driven by phonon.

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Silicon clathrate Na$_8$Si$_{46}$ has been known as a nonsuperconducting metal down to 2 K for more than thirty years. The crystal structure consists of Si$_{20}$ and Si$_{24}$ cages sharing their pentagonal faces with each other, with Na atoms occupying these cages (see Fig. 1). Though the silicon clathrate is reminiscent of the electron-doped C$_{60}$, the intercage bonding makes the clathrate different from the doped C$_{60}$, where individual C$_{60}$ molecules essentially influence its physical properties: Clathrates are covalent crystals, while fullerides are molecular crystals. Motivated by the discovery of the superconductivity in the doped C$_{60}$ compounds with the highest transition temperature (\(T_c\)) exceeding 30 K (Ref. 2) and expectation of higher \(T_c\) even in the silicon clathrates because of expected higher Debye temperatures originating in the rigid sp$^3$ Si-Si covalent bonding, Yamanaka et al. succeeded in synthesizing superconducting Na$_8$Ba$_6$Si$_{46}$ with \(T_c\) of 4 K (Ref. 3). A remarkable point of this success is that this is a superconductor with sp$^3$ Si-Si covalent bonding, implying a possibility of occurring superconductivity in the other cubic-silicon-like sp$^3$ materials. This, along with their physically and industrially interesting properties, has brought about renewed attention, and has stimulated experimental and theoretical studies.

Comparative band structure calculations of Si$_{46}$ and Na$_2$Ba$_6$Si$_{46}$ show that the density of states (DOS) of the conduction band in Na$_2$Ba$_6$Si$_{46}$ is strongly modified compared to that of pristine Si$_{46}$ due to strong hybridization between Si$_{46}$ and Ba states. This modification produces a sharp peak at the Fermi level (\(E_F\)), which is thought to play a crucial role for the superconductivity because of the very high DOS at \(E_F\). Nuclear magnetic resonance (NMR) studies have experimentally confirmed that the existence of the strong hybridization together with partial ionization of Na and Ba in Na$_2$Ba$_6$Si$_{46}$ (Ref. 8), but also discussed somewhat lower DOS at \(E_F\) compared to the value from the calculations. Raman spectroscopy has been performed

![FIG. 1. Schematic structure model of Ba$_8$Si$_{46}$. Ba atoms occupy all of the silicon cages.](image-url)
calculations.\textsuperscript{7,19} But the observed bandwidth (\(\sim 0.3\) eV) of the peak at \(E_F\) is narrower than the calculated bandwidth (\(\sim 1.5\) eV), suggestive of a deviation from one electron approximation. Furthermore, we observe a clear opening of a superconducting gap below \(T_c\) with the gap size of 1.3 meV, which corresponds to a reduced gap size of \(2\Delta(0)/k_B T_c = 3.51\). We also observe fine structures up to \(\sim 70\) meV in superconducting spectrum, whose energy is nearly equivalent to the highest phonon energy for \(\text{Na}_8\text{Si}_{46}\) clathrate.\textsuperscript{16}

These results for the superconducting state classify \(\text{Ba}_8\text{Si}_{46}\) into a weak-coupling superconductor most probably mediated by phonon. These experimental results provide direct information on the electronic structure and superconducting transition of the silicon clathrate superconductor.

\(\text{Ba}_8\text{Si}_{46}\) samples were prepared using a high-pressure synthesis as described in the literature.\textsuperscript{18} \(\text{Ba}_8\text{Si}_{46}\) made by the same procedure has shown superconductivity below 8 K for both resistivity and susceptibility measurements.\textsuperscript{18}

PE measurements were performed on a spectrometer built using a GAMMADAT-SCIENTA SES2002 electron analyzer and a high-flux discharging lamp with a toroidal grating monochromator. The total energy resolutions (analyzer and light) for total valence band measurements using the He \(\alpha\) (21.218 eV) and He \(\text{I}\alpha\) (40.814 eV) resonance lines were set to 70 and 100 meV, respectively, while that for \(E_F\) region was set to 8 meV. Ultrahigh-resolution measurement very close to \(E_F\) for a superconducting gap was done with 2.4 meV resolution. The sample temperatures were measured using a silicon-diode sensor mounted just close to it. The base pressure of the spectrometer was better than \(5 \times 10^{-11}\) Torr. Samples were fractured \textit{in situ} to obtain clean surfaces and all the measurements were done within 3 h after the fractures. We did not see any spectral changes within the time interval, indicating the observed spectra are reflecting intrinsic electronic structures. Temperature dependent spectral changes were confirmed by cycling temperature across \(T_c\). \(E_F\) of samples was referenced to that of a gold film evaporated onto the sample substrate and its accuracy is estimated to be better than \(\pm 0.05\) meV.

Figure 2 shows valence band PE spectra of superconducting \(\text{Ba}_8\text{Si}_{46}\) obtained at 5.4 K using He \(\text{I}\alpha\) and He \(\text{I}\alpha\). The valence band spectrum measured with He \(\text{II} \alpha\) shows a peak at \(E_F\) and several features as shown by vertical lines. Corresponding structures are seen in He \(\text{I}\alpha\) spectrum, though the accessible energy region of He \(\text{I}\alpha\) spectrum is smaller than that of He \(\text{II} \alpha\) due to the smaller photon energy. In Fig. 2, we also show the total DOS obtained from the first principals calculations using local density approximation (LDA) (Ref. 19), incorporating a matrix element effect as well as resolution and lifetime broadening as a Gaussian with full width at half maximum (FWHM) of 0.5 eV. As shown with thin dotted lines, the experimentally observed features beyond 2 eV can be related to those in the calculated DOS. However, well-separated three prominent structures which can be assigned to Si 3s, Si 3s-\(p\), and Si 3\(p\) like states of the Si\(_{46}\) framework in the calculations do not clearly appear in the experimental spectrum. This indicates that the Ba atom influences the Si\(_{46}\) cage more than the expectation from band calculations, supporting the NMR study which confirmed the existence of strong hybridization in \(\text{Na}_8\text{Ba}_3\text{Si}_{46}\).\textsuperscript{16}

Furthermore, we find there is a substantial discrepancy between the present results and calculations especially for the electronic states within 2 eV below \(E_F\). Besides a peak at \(E_F\), we observe a broad hump at 1.5 eV in the observed spectrum, no representative structure of which we see in the calculation. The observed result is reminiscent of that reported for metal-insulator transition systems like V\(_2\)O\(_3\).\textsuperscript{20} As for the peak at \(E_F\), the intensity seems smaller compared to the intensity of the bands at 2–6 eV, while those are similar in the calculation. Further, the width of the peak at \(E_F\) is smaller than that of the calculated one, as shown in the inset of Fig. 2. We see that the peak shows a width of \(\sim 0.3\) eV with fine structures near \(E_F\) (we will discuss this later), while the calculated peak has a width of \(\sim 1.5\) eV. These results indicate that the LDA calculation is not enough for describing the electronic structure of Si clathrate, implying importance of electron correlations which may be expected from the flat bands due to its large unit cell, as in the C\(_{60}\) crystals.\textsuperscript{2} However, in order to address the electron correlation in the silicon clathrates, further studies including resistivity, specific heat, and de Haas–van Alphen measurements will be necessary.

In He \(\text{I}\alpha\) spectrum, we can observe Ba 5\(p_{1/2}\) and 5\(p_{3/2}\) shallow core levels at 17.1 and 15.1 eV binding energies, respectively. The energy position of the Ba 5\(p_{3/2}\) is 15.1 eV.
and found to have a shift of 0.6 eV compared to that of a Ba metal (14.6 eV) (Ref. 21). This value is similar to the shift of $5p_{3/2}$ reported for BaS (0.53 eV) but slightly smaller than that of BaO (0.86 eV) (Ref. 22), in which Ba atoms are believed to take a divalent state. This observation agrees with the NMR measurements$^8$ reporting that the Ba atoms are partially ionized, indicating a covalent-like bonding of Ba atoms and Si$^{46}$ cages.

To study the superconducting electronic structure of Ba$_8$Si$_{46}$, we further performed ultrahigh-resolution measurements. In Fig. 3, we show the results measured at 5.4 K (superconducting state, open circles) and 10.0 K (normal state, open squares) normalized with area under the curve from 12 to −8 meV. The normal state spectrum has a leading edge whose midpoint is nearly located at $E_F$. In contrast, the superconducting-state spectrum exhibits a spectacular redistribution of the spectral intensity from at and above $E_F$ to higher binding energy, forming a new peak around 3 meV. This is a direct measurement of the superconducting gap of silicon clathrates. To obtain the magnitude of the superconducting gap, we have done numerical simulations using the Dynes function, assuming a constant normal-state DOS and using the energy resolution of 2.4 meV. We superimpose a result using $\Delta = 1.3$ meV and $\Gamma = 0.3$ meV (curve), which well reproduces the superconducting spectrum as shown in Fig. 3. From the known temperature dependence of the superconducting gap for both weak- and strong-coupling superconductors, we$^{24}$ we estimate the gap value at 0 K and obtain a reduced gap, $2\Delta(0)/k_BT_c = 3.51$. This classifies Ba$_8$Si$_{46}$ into a weak-coupling superconductor. We note that this value is similar to those obtained for K$_2$C$_{60}$ and Rb$_2$C$_{60}$ (3.53) using photoemission spectroscopy.$^{25}$

Lastly, we turn to the structures near $E_F$ but in slightly wider regions as shown in Fig. 4. First we emphasize that the

FIG. 3. Ultrahigh-resolution PE spectra of Ba$_8$Si$_{46}$ measured at 5.4 K (superconducting state, open circles) and 10.0 K (normal state, open squares) using an energy resolution of 2.4 meV. A curve superimposed on the superconducting spectrum is the result of a numerical calculation using the Dynes function with $\Delta = 1.3$ meV and $\Gamma = 0.3$ meV.

FIG. 4. High-resolution PE spectrum of Ba$_8$Si$_{46}$ using an energy resolution of 8 meV (open circles) together with a smoothing curve demonstrating existence of fine structures. Arrows are representing the positions of a weak dip ($\sim 50$ meV) and a maximum ($\sim 30$ meV) in the intensity.

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2 For review, see O. Gunnarson, Rev. Mod. Phys. 69, 575 (1994).


20 For review, see M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).


