Evidence for Scattering-Dependent Multigap Superconductivity in Ba$_8$Si$_{46}$

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We have studied the quasiparticle excitation spectrum of the superconductor Ba$_8$Si$_{46}$ by local tunneling spectroscopy. Using high energy resolution achieved in Superconductor-Superconductor junctions we observed tunneling conductance spectra of a non-conventional shape revealing two distinct energy gaps, $\Delta_L = 1.3 \pm 0.1$ meV and $\Delta_S = 0.9 \pm 0.2$ meV. The analysis of tunneling data evidenced that $\Delta_L$ is the principal superconducting gap while $\Delta_S$, smaller and more dispersive, is induced into an intrinsically non-superconducting band of the material by the inter-band quasiparticle scattering.

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In their microscopic theory of superconductivity [1] Bardeen, Cooper and Schrieffer (BCS) predicted the existence of a single gap $\Delta = cte$ in the elementary excitation spectrum of a superconductor (SC). However, already in late 60s, some SCs from the A15 family did show anomalies in specific heat that could be attributed to the presence of several energy gaps [2,3]. The existence of two energy gaps has also been suggested for Nb, Ta and V [4]. Recent discovery of the two distinct SC gaps in MgB$_2$ reported in specific heat [5] and Scanning Tunneling Microscopy/Spectroscopy (STM/STS) experiments [6,7], with the excitation spectrum deviating from the BCS, strongly renewed the interest for non-standard SCs [8-11].

Among the covalent sp$^3$ materials, like silicon carbide or silicon (or carbon) diamond, the silicon clathrate Ba$_8$Si$_{46}$ appears to be a good candidate for a non-conventional superconductivity. This doped clathrate is formed by covalent Si$_{20}$ and Si$_{24}$ cages sharing their faces and filled with intercalated Ba atoms (for more details, see [12]). It has been shown that the superconductivity appearing in Ba$_8$Si$_{46}$ at $T_c = 8.1$ K [13,17] is mediated by phonons and is an intrinsic property of the sp$^3$ network formed by Si atoms [10]. Eight encaged Ba atoms per unit cell provide the charge carriers resulting in a complex band structure with several bands crossing the Fermi level. Thus, one could expect the superconductivity to appear in two or more bands, and to depend on the inter-band scattering. Up to now, the question remained a subject of controversy: K. Tanigaki et al. concluded on a conventional BCS superconductivity in Ba$_8$Si$_{46}$ [17], while tunneling spectroscopy data evidenced for an anisotropic order parameter [19], and recent results of specific heat measurements were reported to be consistent with two-gap superconductivity [11].

In this Letter we report the local tunneling spectroscopy (TS) of Ba$_8$Si$_{46}$ performed in the STM geometry. In order to enhance the energy resolution, we studied Superconductor-Vacuum-Superconductor (SIS) tunneling junctions formed by in-situ cleaved Ba$_8$Si$_{46}$ grains (used as STM tips) [6] and a clean surface of 2H–NbSe$_2$ or, alternatively, another grain of Ba$_8$Si$_{46}$, used as a "sample". Statistical analysis of SIS spectra revealed two energy gaps to exist in Ba$_8$Si$_{46}$, a large one $\Delta_L = 1.3 \pm 0.1$ meV, giving a ratio $2\Delta_L/kT_c = 3.7 \pm 0.3$ matching the BCS value, and a smaller one $\Delta_S = 0.9 \pm 0.2$ meV. This apparent small gap is interpreted as being due to the inter-band scattering induced superconductivity in an intrinsically non-superconducting electronic band of Ba$_8$Si$_{46}$.

Polycrystalline Ba$_8$Si$_{46}$ samples were synthesized at high pressure and temperature [12,18]. The Ba$_8$Si$_{46}$ tips were fabricated by gluing a small grain of the material at the apex of a standard Pt/Ir tip. The grains were then fractured prior TS experiment in order to expose a clean surface facing the STM junction (see inset in Fig.1b). In this work, both ex-situ and in-situ fractured Ba$_8$Si$_{46}$-tips were studied. As a control of the tip quality, the ability of the tips to image Au or NbSe$_2$ surfaces was systematically checked. We also visualized the vortex lattice in NbSe$_2$ and observed the voltage dependent contrast (Fig.1a) expected for high-quality SIS junctions [20]. These evidence both the vacuum tunneling regime and the clean surfaces of the tunneling electrodes. The raw $I(V)$ data acquired at tunneling resistances 10-100M$\Omega$ were numerically derived, and the resulting $dI(V)/dV$ spectra are presented normalized to unity for clarity.

Fig.1b presents typical SIN tunneling conductance spectra obtained with Ba$_8$Si$_{46}$ tips on Au. The spectra exhibit a smooth apparent gap $\Delta_{Ba_8Si_{46}} \simeq 1.0$ meV with no additional spectroscopic features visible. The position of the peaks slightly varies (typically $\pm 0.2$ mV) from one
and the non conventional shape of the tunneling spectra
with a Ba

Two typical SIN tunneling conductance spectra obtained
from the anisotropy
tip from Au film (red and blue dots). Solid
line: best fits using the McMillan equations (2) with \( \Delta_1 = 0.08 \) (0.05) meV, \( \Gamma_1 = 10 \) (11) meV, \( \Delta_2 = 1.2 \) (1.33) meV, \( \Gamma_2 = 1.49 \) (1.31) meV for red (blue) curve; inset: schematic
drawing of the experimental geometry. c) BaSi46 vs NbSe2 SIS spectra (\( T = 2.2 \) K) reveal two distinct energy gaps in
BaSi46 (showed with down arrows): \( \Delta_S \approx 0.8 \) meV (blue curve) and \( \Delta_L \approx 1.4 \) meV (red curve). d) BaSi46 vs BaSi46 SIS tunneling conductance spectrum (blue curve). Red line: SIS fit with BCS clearly fails to reproduce the observed large quasiparticle peaks and dips (pointed with arrows).

FIG. 1: (Color online) a) Vortex lattice in NbSe2 at \( B = 0.165 \) T revealed with BaSi46 tips at the biases (from left to right) \(-2.0\) mV, \(-0.9\) mV, \(+1.0\) mV, \(+1.9\) mV shows the contrast inversion characteristic to SIS junctions [21]. b) Two typical SIN tunneling conductance spectra obtained with a BaSi46 tip on Au film (red and blue dots). Solid lines: best fits using the McMillan equations (2) with \( \Delta_1 = 0.08 \) (0.05) meV, \( \Gamma_1 = 10 \) (11) meV, \( \Delta_2 = 1.2 \) (1.33) meV, \( \Gamma_2 = 1.49 \) (1.31) meV for red (blue) curve; inset - schematic
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SIS spectra. The necessity of a precise description of realistic SCs
requires the consideration of realistic SCs
which were interpreted as resulting from the anisotropy
of BaSi46 - NbSe2 SIS spectra and their geometrical (Fig1b).
The best BCS fit (red solid line in Fig1d) gives \( \Delta_{BaSi46} = 1.04 \) meV. Thus, both SIN and SIS data in Fig1 reveal \( \Delta_{BaSi46} \approx 0.9 \pm 0.2 \) meV, too low to account alone for the superconductivity in bulk BaSi46 (2\( \Delta_{BaSi46} / kT_c = 2.6 < 3.52 \)). Furthermore, the standard BCS fit (red line in Fig1d) fails to account for strongly broadened quasiparticle peaks and local minima - dips [21]. Both the low gap energy and the non conventional shape of the tunneling spectra
suggest the existence of another (hidden) leading SC gap \( \Delta_2 \) responsible for the superconductivity in BaSi46.

The necessity of a precise description of realistic SCs
stimulated an important piece of theoretical effort. In 1959 Suhl, Matthias and Walker [22] extended the one-band isotropic BCS model to the case of two energy bands. Such a two-band SC exhibits two distinct gaps in its excitation spectrum, \( \Delta_1 \) and \( \Delta_2 \). Analytically, the tunneling DOS is the weighted sum of two BCS spectra
for in the model above, leads to an additional modification of the quasiparticle excitation spectrum [23]. The latter may be calculated considering two initial BCS gaps in each band \( \Delta_0 \) and \( \Delta_2 \), and the coupling energies \( \Gamma_1 \) and \( \Gamma_2 \) accounting for the quasiparticle scattering from one band to another. Similarly to the case of the proximity effect in the real space developed by McMillan [24], one obtains two coupled equations for the energy dependent effective gaps \( \Delta_1(E) \) and \( \Delta_2(E) \):

\[
\Delta_1(E) = \frac{\Delta_1^0 + \Gamma_1 \Delta_2(E) / \sqrt{\Delta_2^0(E) - (E - i \Gamma_2)^2}}{1 + \Gamma_1 / \sqrt{\Delta_2^0(E) - (E - i \Gamma_2)^2}}
\]

\[
\Delta_2(E) = \frac{\Delta_2^0 + \Gamma_2 \Delta_1(E) / \sqrt{\Delta_1^0(E) - (E - i \Gamma_1)^2}}{1 + \Gamma_2 / \sqrt{\Delta_1^0(E) - (E - i \Gamma_1)^2}}
\]

These equations allow one to calculate the tunneling spectrum of a two-band SC, by replacing the constant gaps \( \Delta_i \) in (1) by the energy dependent gaps \( \Delta_i(E) \) [23].

In Fig 2a,b we present SIN tunneling spectra, Fig 2c showing their evolution with temperature. The enhanced energy resolution of SIN spectroscopy revealed the apparent gap \( \Delta_{BaSi46} \) to vanish exactly at the \( T_c \) of the bulk material, thus evidencing its relation to the bulk SC (Fig 2d). The SIS fits using eqs. (2) (solid lines in Fig 2) reproduce in fine details the shape of the SIN tunneling conductance data, with different counter electrode materials (in the case of NbSe2, Fig 2a, the exact DOS was taken from [27]) and at various temperatures (red lines in Fig 2c). A perfect agreement is also achieved when fitting SIN spectra (solid lines in Fig 1b). By analyzing the fitting parameters of different tunneling spectra we noticed the following common features: i) for all spectra initial BCS gap in the band \( i = 1 \) is \( \Delta_0^i \approx 0 \) while \( \Delta_2^i = 1.3 \pm 0.1 \) meV. ii) the interband scattering parameters, \( \Gamma_1 \) and \( \Gamma_2 \) strongly vary from one junction to
another, but their ratio remains almost fixed $\Gamma_1/\Gamma_2 \sim 10$ (see also Fig.3d). iii) for most of the studied junctions the tunneling contribution of the band $i = 1$ was $W_1 = 1$ and that of $i = 2$ was $W_2 = 0$, i.e. we needed only the term $N_{S1}(E)$ to fit the tunneling spectra. Thus, only two really free parameters remained, $\Delta^0_2$ and $\Gamma_1(\Gamma_2)$. Moreover, the fits in Fig.2c were generated considering only one free parameter, $\Delta^0_2$, the second being evaluated at $T = 2.2 \text{K} (\Gamma_1 = 10 \Gamma_2 = 6 \text{meV})$ and kept fixed.

Let us now discuss the physics behind such a surprisingly nice agreement between the data and fits, and analyze the consequences of the above mentioned common features. The condition $\Delta^0_1 \approx 0 \text{meV}$ implies that the superconductivity in the band $i = 1$ is fully induced: a small gap opens in $N_{S1}(E)$ due to the coupling with the leading superconducting band $i = 2$ where the pairing amplitude $\Delta^0_2 \approx 1.3 \text{meV}$ is found close to the value 1.4 meV estimated from specific heat measurements [11]. The observed fluctuations of the induced small gap $\Delta_S$ from one junction to another, $\pm 0.2 \text{meV}$, are attributed to the variations of both the scattering rates $\Gamma_i$ and the pairing amplitude of the initial gap $\Delta^0_i$. Besides, a larger scattering due to the surface disorder may explain the differences between $\Delta_S$ observed in TS data and the one (0.35 meV) found in specific heat measurements [11]. Indeed, the value $\Delta_S = 0.35 \text{meV}$ can be easily calculated with (2) considering a smaller $\Gamma_1 = 0.6 \text{meV}$ in the bulk.

A clear linear correlation between $\Gamma_1$ and $\Gamma_2$ is evidenced in Fig.3d, with $\Gamma_1/\Gamma_2 \sim 10$. This result is consistent with the scattering in a two-band material: The interband scattering events $1 \rightarrow 2$ and $2 \rightarrow 1$ should be equal and therefore the condition $\Gamma_1/\Gamma_2 = N_2(E_F)/N_1(E_F)$ must be fulfilled [22]. The ratio $\sim 10$ we find is in very good agreement with the value $N_2(E_F)/N_1(E_F) = 9$ determined from specific heat measurements [11], that strongly supports our model. Concerning the variations of $\Gamma_1$ and $\Gamma_2$ observed in different experiments, we relate them to the specific scattering conditions due to the local surface disorder, realized for each junction [22].

In Figs.3a and 3b we show the partial DOSs $N_{Si}(E)$ calculated for bands $i = 1$ and $i = 2$ respectively. We took $\Delta^0_1 = 0 \text{meV}$ and $\Delta^0_2 = 1.3 \text{meV}$, different curves corresponding to the coupling parameters $\Gamma_i$ varying from 0.5 to 15 meV with a constant ratio $\Gamma_1/\Gamma_2 = 10$. As a result of the inter-band quasiparticle scattering, a gap $\Delta_S$ is induced in the first band where it does not exist at zero coupling. The DOS shape in the first band is very peculiar (Fig.3a): The quasiparticle peaks are broadened and there are some shoulders at the position of the large gap peaks. This peculiar shape is responsible of the dips in SIS spectra, experimentally observed. Broad peaks and dips are also observed in high-$T_c$ SCs and attributed to the coupling with a collective excitation mode [20]. Their amplitudes and the characteristic energies (normalized to the $T_c$) are however much higher as compared to our case. In the second band, Fig.3b, the initially pure BCS DOS evolves with the coupling: A mini-gap (often called ‘excitation gap’) appears at the same position that the induced gap in the first band. The evolution of the gaps $\Delta_L$ and $\Delta_S$ in the partial DOSs with the coupling parameter $\Gamma_1$ is presented in Fig.3c. Both gaps vary strongly at moderate $\Gamma_1$ and reach the same asymptotic value for very large coupling, where one recovers a simple one-gap BCS DOS.

In the search for a direct evidence of the large gap $\Delta_L$, we studied several tens of Ba$_8$Si$_{46}$ tips and acquired the SIS spectra in thousands of locations, similar to what was done in the case of MgB$_2$ [21]. We expected that the surface defects such as large steps, protrusions, holes would provide various tunneling conditions. In some measurements we indeed observed very different still reproducible SIS spectra (red curve in Fig.1c), while keeping the tunneling conditions unchanged. They show no dips, as expected for SIS spectra revealing the large gap, Fig.3b. Furthermore, the gap energy $\Delta_L \approx 1.4 \text{meV}$ correspond-
FIG. 3: (Color online) Partial DOSs in the band 1 in (a) and 2 in (b) calculated within the McMillan model with \( \Delta_1^0 = 0 \), \( \Delta_2^0 = 1.3 \text{ meV} \), \( \Gamma_1 = 0.5, 1, 2, 5, 15 \text{ meV} \), \( \Gamma_2 = \Gamma_1/10 \). (c) Evolution of the excitation gap and apparent gaps \( \Delta_L, \Delta_S \) with the scattering rate \( \Gamma_1 \), corresponding to (a) and (b). (d) Scatter plot of the fit parameters \( \Gamma_2 \) vs \( \Gamma_1 \). Red line: linear dependence \( \Gamma_2 = \Gamma_1/10 \).

ing to these spectra is in a good agreement with the large gap deduced from specific heat measurements by Lortz et al. [11].

It is not fully established for the moment why the spectra revealing directly the large gap are so rare. In the case of MgB\(_2\) a similar statistics was observed and attributed to the low probability of tunneling into the two-dimensional \( \pi\)-band. It is not clear if such an assumption holds for Ba\(_8\)Si\(_{46}\). We know however that in Ba\(_8\)Si\(_{46}\) most of the DOS belongs to Ba-Si hybridized states located inside the Si cages [17, 18]. It couples well to Ba phonon rattling modes that contribute to the SC pairing [11, 30]. Hence, we may speculate that the electronic states responsible for the superconductivity are somehow confined inside the clathrate cages, and the amplitude of the corresponding evanescent waves outside the material is thus weak, leading to a tiny contribution into the tunneling. Consequently, most of the tunneling current comes from the outer-cage Si orbitals where the superconductivity is purely induced.

Finally, we have studied the quasiparticle excitation spectrum of the superconductor Ba\(_8\)Si\(_{46}\) by local tunneling spectroscopy. Owing high energy resolution achieved in SIS junctions we resolved fine spectroscopic features that cannot be accounted for by BCS. The SIS spectra evidence the existence of two distinct energy gaps, \( \Delta_L = 1.3 \pm 0.1 \text{ meV} \) and \( \Delta_S = 0.9 \pm 0.2 \text{ meV} \), that are interpreted in terms of a two-band superconductivity in Ba\(_8\)Si\(_{46}\) characterized by a leading gap \( 2\Delta_L/kT_c = 3.7 \pm 0.3 \) and another, smaller coupling-dependent gap \( \Delta_S \), reflecting the superconductivity induced in an intrinsically non-superconducting electronic band.

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