Large enhancement of superconductivity in Zr point contacts

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Received 17 January 2018, revised 19 April 2018
Accepted for publication 30 April 2018
Published 1 June 2018

Abstract

For certain complex superconducting systems, the superconducting properties get enhanced under mesoscopic point contacts made of elemental non-superconducting metals. However, understanding of the mechanism through which such contact induced local enhancement of superconductivity happens has been limited due to the complex nature of such compounds. In this paper we present a large enhancement of superconducting transition temperature $T_c$ and superconducting energy gap $\Delta$ in a simple elemental superconductor Zr. While bulk Zr shows a critical temperature around 0.6 K, superconductivity survives at Ag/Zr and Pt/Zr point contacts up to 3 K with a corresponding five-fold enhancement of $\Delta$. Further, the first-principles calculations on a model system provide useful insights. We show that the enhancement in superconducting properties can be attributed to a modification in the electron–phonon coupling accompanied by an enhancement of the density of states which involves the appearance of a new electron band at the Ag/Zr interfaces.

Keywords: zirconium, point contact, superconductivity, spectroscopy, Andreev reflection

(Some figures may appear in colour only in the online journal)
by first principles calculations. Based on our calculations we conclude that in case of Zr, the enhancement can be attributed to two factors: (a) a significant enhancement of the DOS at the Fermi surface which is also associated with the emergence of a new electron-band at the Fermi surface, and (b) a substantial increase in the electron–phonon coupling \cite{23} under the point contacts, as compared to bulk Zr.

The low-temperature experiments were performed in a He\textsuperscript{3} cryostat working down to 500 mK using a home-built point-contact spectroscopy probe. The probe is equipped with a piezo walker that facilitates fine adjustment of the tip–sample distance. The entire measurement system including the tip and the sample go to the center of a solenoidal magnet working up to 7 T. In figure 2 we show point contact spectra obtained for (a) and (c) Ag/Zr and (b) and (d) Pt/Zr point contacts. At the lowest temperature (0.5 K), the $dI/dV$ versus $V$ spectra show a central peak followed by two dips symmetric about $V = 0$. These spectral features indicate that the point contact is in the thermal regime of transport where the dips appear due to the critical current of the superconducting point contacts. All these features systematically evolve with increasing magnetic field and the features disappear at 1.6 K for Ag/Zr point contacts and at 2.3 K for Pt/Zr point contacts. Temperature dependent measurements of the normal state resistance of these point contacts reveal superconducting transitions at 1.6 K (for Ag/Zr) and 2.8 K (for Pt/Zr) respectively (refer to figure 1). These values are significantly larger than the known bulk critical temperature of Zr (0.57 K). The transition temperature goes down with increasing magnetic field, as expected for superconducting point contacts. We believe, for Pt/Zr point contacts, the spectral features disappear at a temperature lower than the resistive transition temperature due to associated thermal broadening of spectral features. The spectral features shown in figures 2(a) and (b) also fade away with increasing magnetic field.

Though the critical temperature of the superconducting point contacts can be accurately estimated from the thermal regime data presented above, for the determination of superconducting energy gap ($\Delta$), the experiments must be performed in the ballistic or diffusive regime of transport where energy resolved spectroscopy is possible through Andreev reflection spectroscopy. We have driven the point contacts away from the thermal regime by reducing the diameter of the point contacts \textit{in situ}. As shown in figures 3(a) and (c), we have obtained data in a regime where clear features (two conductance peaks symmetric about $V = 0$) associated with Andreev reflection appear. These data have also been fitted well by the model developed by Blonder, Tinkham and Klapwijk (BTK) \cite{24}. The BTK fits reveal a superconducting energy gap of 0.51 meV for Pt/Zr point contacts indicating $\Delta/k_BT_c = 1.74$, which is consistent with weak-coupling BCS prediction confirming that even above the bulk $T_c$ of Zr, the superconducting region confined under point contact remains conventional in nature. The Andreev reflection spectra evolve systematically with both temperature (figure 3(a)) and magnetic field (figure 3(b)). BTK analysis of the temperature dependent spectra confirm the BCS temperature dependence of the superconducting energy gap. The superconducting energy gap also decreases systematically with increasing magnetic field (figure 3(d)).

In order to gain some useful insight into the experimental observations in a tractable fashion, we have modelled the
Figure 2. Temperature dependence of thermal limit spectra on (a) Ag/Zr and (b) Pt/Zr point-contacts. Magnetic field dependence of thermal limit spectra on (c) Ag/Zr and (d) Pt/Zr point-contacts.

Figure 3. (a) Temperature dependence of the intermediate regime spectra on Pt/Zr point-contact. (b) Temperature dependence of the superconducting gap amplitude extracted from fitting the data following the BTK theory. (c) Magnetic field dependence of the intermediate regime spectra on Pt/Zr point-contact. (d) Variation of the superconducting gap amplitude with magnetic field strength extracted from fitting the data following the BTK theory.
macroscopic point contact on Zr surface through superlattice calculations. As the diameter of the point contact is \(\sim 100\ \text{nm}\), such a reduced structural model remains valid, at least under the first approximation. A similar approach has been reported to model the interaction of a mesoscopic tip with a surface in the context of superconductivity [25]. The electronic structure calculations were performed within norm-conserving Troullier–Martins pseudopotential scheme [26] and local-density approximation [27, 28] implemented in QUANTUM ESPRESSO code [29]. The Kohn–Sham wave functions and charge density were expanded in the plane wave basis with energy cutoffs of 60 and 240 Ry. Structures were fully relaxed until the forces on each atom were smaller than 10\(^{-4}\) Ry \(\text{Å}^{-1}\) using 12 \times 12 \times 8 Monkhorst–Pack \(k\)-mesh [30] with 0.02 Ry Methfessel–Paxton smearing for electronic state occupancy [31]. Highly dense \(k\)-point grid of 60 \times 60 \times 60 was used to calculate Fermi surfaces. Dynamical matrices are calculated on a 6 \times 6 \times 4 \(q\)-mesh in the Brillouin zone using density functional perturbation theory [32]. Further, the electron–phonon (\(e-p\)) coupling was calculated using the electron–phonon Wannier method [33] as implemented in the EPW code [34]. Maximally localized Wannier functions are constructed on a 6 \times 6 \times 4 \(k\)-mesh using Wannier90 code [35–37]. Finally, fine electron 24 \times 24 \times 16 \(k\)-grid and phonon 24 \times 24 \times 16 \(q\)-grids with phonon smearing 0.3 meV were used to calculate Eliashberg spectral function. To investigate the effects of metallic Ag point contact on the (0001)-Zr surface, we considered a periodic 2 \times 2 \times 2 ZrAg superlatice. The corresponding superlattice was completely relaxed, which results in chemical Zr–Ag bond formation with 2.89 Å distance. Note that the interlayer distance between the tip and surface is completely relaxed, which results in 2.3 Å vertical separation. Therefore, for the present model calculation, the repeating Zr layers are separated by 7 Å distance, which is sufficient to exclude their interaction. Due to the influence of the tip, the in-plane Zr–Zr distance for the (0001)-Zr surface is contracted to 3.03 Å compared to 3.23 Å in the corresponding bulk structure.

Phonon mediated superconductivity is well described by Migdal–Eliashberg theory and the corresponding \(T_c\) is
exp\[\ln 1 + \omega \alpha\] = \omega_{A}\), which are shown in figure 5(a). In addition to the Fermi level. Further, the Coulomb repulsion, and should be in the range \(\mu^* = 0.1 - 0.2\) [40, 41]. In the present case, we assumed \(\mu^* = 0.18\), which provides a closer agreement with the experimental \(T_c\) for the bulk hcp Zr. Due to the lack of a definite first-principles approach to evaluate \(\mu^*\), we kept it fixed for the superlattice representing the Ag-tip on Zr-surface. The Eliashberg spectral function for the \(e-p\) interaction is obtained as [42, 43],

\[
\alpha^2 F(\omega) = \frac{1}{N(E_F)} \sum_{k,\gamma} |G_{k,\gamma}|^2 \delta(\epsilon_k)\delta(\epsilon_{k+q})\delta(\omega - \omega_{\gamma}),
\]

(2)

where \(N(E_F)\) is the electronic density of states (DOS) at the Fermi level, \(\omega_{\gamma}\) is the phonon frequency of wave vector \(q\) and mode \(\gamma\). The \(G_{k,\gamma}\) is the \(e-p\) matrix element for the scattering of electron between states with momenta \(k\) and \(k+q\) at the Fermi level. Further \(\lambda\) and \(\omega_{\gamma}\) are obtained using \(\alpha^2 F(\omega)\) as \(\lambda = 2 \int \alpha^2 F(\omega) d\omega\) and \(\omega_{\gamma} = \exp[\frac{1}{\lambda} \int \alpha^2 F(\omega) \ln(\omega) d\omega]\).

We first discuss the picture for pure hcp-Zr, and subsequently investigate the effects of elemental Ag-tip. In figure 4(a), the decomposed band structure of hcp-Zr along the high-symmetry directions of Brillouin zone indicate two hole-like bands centered at the \(\Gamma\)-point, which originate mainly from the Zr-\(d\) orbitals, while the Zr-\(p\) contribution at the Fermi level is negligible. These two bands become doubly degenerate at \(A\)-point. The corresponding Fermi surface (FS) consists of two cylindrical hole like sheets (figures 4(c) and (d)) and the electronic DOS at \(E_F\) is found to be 1.84 states/(eV-unit-cell) (figure 4(a)). The introduction of Ag-tip substantially perturbs the Zr band structure (figure 4(b)), which comprises of three hole pockets and one electron pocket. While the electrons around \(K\)-point and the hole pocket at \(\Gamma\) are comparable in size, the hole pockets between \(A - L\) are found to be much smaller. Further, the size of the hole pocket at \(\Gamma\) is larger in size (figure 4(e)) compared to pure-Zr, and the electron pockets at \(K\) are connected by a tubular network (figure 4(f)). Due to the insertion of Ag-tip, the Zr-DOS at \(E_F\) is increased by about 62% to 2.98 states/(eV-unit-cell) (figure 4(b)). In contrast, a small contribution of 0.46 states/(eV-unit-cell) is contributed from the Ag-tip. This picture is further confirmed through the orbital projected band structure in figures 4(h) and (i), which indicate that states around the \(E_F\) are mainly derived from the Zr-\(d\) orbitals. Next, we compare the phonon dispersion and DOS without and with the tip (supplementary material). We do not observe any kinetic instability due to Ag-tip insertion, and interestingly observe softening of the acoustic modes and the additional appearance of many optical modes in the presence of tip.

In order to quantify the interaction between electrons and phonons, we calculate \(\alpha^2 F(\omega)\) and total \(e-p\) coupling \(\lambda(\omega \rightarrow \infty)\), which are shown in figure 5(a). In addition to increased spectral weight, more peaks in \(\alpha^2 F(\omega)\) between 5–25 meV indicate more phonons to couple with electrons and enhance \(e-p\) coupling. Further, we have calculated the Fermi surface nesting function \(\xi_q = \sum_k \delta(\epsilon_k)\delta(\epsilon_{k+q})\) [44, 45]. For all \(q\)-vectors inside the Brillouin zone, the calculated \(\xi_q\) is substantially enhanced under the influence of Ag-tip (figure 5(b)). Thus, increased electronic DOS, phonon softening along with increased phonon DOS, and substantial increase in \(\xi_q\) together contribute to increase in \(\lambda\). Consequently, \(\lambda(\omega \rightarrow \infty)\) is increased by \(\sim 67%\) to 0.87 for the hcp-Zr/Ag-tip from 0.52 in pure hcp-Zr, which leads to substantial enhancement in the superconducting temperature (table 1).

In conclusion, we have shown that superconductivity of Zr gets dramatically enhanced under metallic point contacts. We observed a large five-fold enhancement of superconducting critical temperature with an associated enhancement of superconducting energy gap. Our first-principles calculations provide useful insights, which indicate that the enhancement in

| \(T_c (K)\) | \(\omega_{\ln} (K)\) | Theory | Experiment |
|----------------|----------------|--------|------------|
| 0.52           | 166            | 0.51   | 0.57       |
| 0.87           | 114            | 3.52   | 3.2        |

Table 1. Measured and calculated superconducting temperature using the Allen–Dynes modified McMillan formula, which is substantially enhanced under metallic point contact through increase in \(e-p\) coupling. The theoretical \(T_c\) is calculated using \(\mu^* = 0.18\).
superconducting temperature is caused by the enhanced density of states and altered electron–phonon coupling under the mesoscopic metallic point contacts.

Acknowledgments

GS acknowledges financial support from a grant awarded by SERB, DST under the grant number EMR/2015/001650. MA thanks CSIR for senior research fellowship (SRF). We acknowledge support from supercomputing facilities at the Centre for Development of Advanced Computing, Pune; Centre for Computational Materials Science, Institute of Materials Research, Tohoku University. M K acknowledges funding by NIT, Government of India under Ramanujan Fellowship, and Nano Mission project SR/NM/TP-13/2016.

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