Supporting Information: Conductance Spectroscopy of Exfoliated Thin Flakes of $Nb_xBi_2Se_3$

C. Kurter,[*,†,‡] A. D. K. Finck,[‡,¶] E. D. Huemiller,[‡] J. Medvedeva,[†] A. Weis,[‡] J. M. Atkinson,[‡] Y. Qiu,[†] L. Shen,[†] S. H. Lee,[†] T. Vojta,[†] P. Ghaemi,[§,‖] Y. S. Hor,[†] and D. J. Van Harlingen[‡]

†*Department of Physics and Materials Research Center, Missouri University of Science and Technology, Rolla, MO 65409*

‡*Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801*

¶*Current address: IBM Thomas J. Watson Research Center*

§*Department of Physics, City College of New York, CUNY, New York, NY 10031*

‖*Department of Physics, Graduate Center of CUNY, New York, NY 10016*

E-mail: kurterc@mst.edu

I. Electronic Band Calculations

The observation of multiple gap-like features and coherence dips in some of the measured differential conductance spectra led us to consider that these spectral features might be due to the existence of multi-band superconductivity. We calculated band structures of Bi_2Se_3 and Nb-intercalated Bi_2Se_3 slabs by using using first-principles density-functional approach, namely, the generalized gradient approximation in the Perdew-Burke-Ernzerhof

form[1,2] within the projector augmented-wave method[3,4] as implemented in the Vienna Ab-Initio Simulation Package (VASP).[5–7]

To study 2D structures under periodic boundary conditions, a vacuum layer with a thickness of 5 Å was inserted to avoid the interaction between the periodic slabs of 2×2 rhombohedral Bi_2Se_3 with three quintuple layers.[8] A dispersion correction of the total energy (DFT-D3 method)[9] was used to simulate the long-range van der Waals interaction between the quintuple layers. A single Nb atom (shown in orange in Fig. 1a) was added either at the surface, inside the top quintuple layer, or between the top two quintuple layers. For the given geometry, the distance between the Nb atoms within the ab plane is 8.3 Å in each case. All the structures were fully relaxed until the Hellmann-Feynman force on each atom was below 0.01 eV/Å . For the geometry optimization and the electronic structure calculations, the cut-off energy of 500 eV and the 8x8x4 Γ-centered k-point mesh were used. The atomic structure of Nb intercalate Bi_2Se_3 slab was plotted using VESTA software.[10]

The energetically preferred location of a single Nb atom within the Bi_2Se_3 slab was determined using the total energy calculations. Similar to the previous investigations for Nb-intercalated bulk Bi_2Se_3,[11] it is found that Nb prefers to be located between the quintuple layers of the Bi_2Se_3 slab. For the cases of an interstitial Nb within the top quintuple layer or of a Nb atom at the surface, the corresponding total energy was found to be higher by 1.13 eV and 1.48 eV, respectively, as compared to that for the intercalate Nb.

For comparison, we first calculated the electronic band structure of Bi_2Se_3 slab without Nb intercalation (see Fig. 1c). As expected, the presence of surface results in the splitting of both the valence and conduction bands near the Γ point. Specifically, it is found that the valence band maximum is composed primarily by the states of the surface Bi_2Se_3 layers (top and bottom layers in the slab), whereas the states of the middle quintuple layer are nearly 0.25 eV lower in energy. The states of all three quintuple layers contribute nearly equally at the bottom of the conduction band at Γ point. Only the states of the surface quintuple layers contribute to the second conduction band (0.2 eV above the conduction band minimum) and

only the states of the middle quintuple layer contribute to the third conduction band (0.4 eV above the conduction band minimum).

The electronic band structure for Nb intercalate Bi_2Se_3 slab was calculated next. The magnetic solution for this atomic configuration was found to be 154 meV lower as compared to the non-magnetic case. The magnetic moment on Nb atom was calculated to be equal to 1.27 μ_B, which is slightly larger than the local magnetic moment of Nb in bulk Bi_2Se_3.[11] Intoduction of Nb into the slab dramatically changes the band structure as shown in Fig. 1(d). The occupied Nb states appearing within the band gap of Bi_2Se_3 below the Fermi energy are highlighted in red and blue; one can see three states for spin-up case and one state for spin-down case. More importantly, Nb states hybridize with the host Bi_2Se_3 states near the Fermi level resulting in a spin-dependent band structure. The spin-resolved differences near Fermi level- as evidenced from the spin-resolved electronic band structure as well as spin-resolved charge density distribution plots in Fig. 1(b)- suggest previously observed multiple Fermi surfaces[12] for Nb-intercalated Bi_2Se_3, which supports our experimental observations of Andreev conductance spectra with multiple gap features.

II. Zero bias conductance

A superconducting device can be treated as a circuit consisting of a resistive element and a superconducting (zero voltage) element. For such a circuit, a finite critical current can generate the appearance of a zero bias conductance peak. When the bias current exceeds the critical current of the superconductor, the device becomes resistive and increases the total circuit resistance. In this picture, the zero bias resistance is equal to that of the resistive element in series with the superconductor, such as contact resistance. We do not expect contact resistance to be strongly dependent on temperature or magnetic field, although the critical current is expected to vary with respect to either such variable. Thus, one would expect the width of the apparent zero bias conductance peak to narrow with increased

temperature or magnetic field, but its height should be essentially unchanged.

In Figs. 3(e) and (f), we show color plots of dI/dV vs V as a function of temperature and magnetic field from an Andreev reflection device made with 16 nm thick flake with low contact resistance. We find that zero bias conductance drops steadily with finite temperature or magnetic field, even as the conductance dips at finite bias remain visible. This is in contrast with the simple picture of the zero bias conductance peak originating from finite critical current and supports the hypothesis that the peak is a signature of low energy bound states.[13]

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