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Unconventional Andreev reflection on the quasi-one-dimensional superconductor $\text{Nb}_2\text{Pd}_x\text{Se}_5$

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We have carried out Andreev reflection measurements on point contact junctions between normal metal and single crystals of the quasi-one-dimensional (Q1D) superconductor $\text{Nb}_2\text{Pd}_x\text{Se}_5$ ($T_c \sim 5.5$ K). The contacts of the junctions were made on either self-cleaved surfaces or crystal edges so that the current flow directions in the two types of junctions are different, and the measurements provide a directional probe for the order parameter of the superconductor. Junctions made in both configurations show typical resistances of ~ 20 - 30 Ohms, and a clear double-gap Andreev reflection feature was consistently observed at low temperatures. Quantitative analysis of the conductance spectrum based on a modified Blonder-Tinkham-Klapwijk (BTK) model suggests that the amplitudes of two order parameters may have angular dependence in the a - c plane. Moreover, the gap to transition temperature ratio (Δ/T_c) for the larger gap is substantially higher than the BCS ratio expected for phonon-mediated s -wave superconductors. We argue that the anisotropic superconducting order parameter and the extremely large gap to transition temperature ratio may be associated with an unconventional pairing mechanism in the inorganic Q1D superconductor. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4947298>]

Many properties of superconductors can be directly attributed to pairing of electrons through electron-phonon interaction which has been well described by the Bardeen-Cooper-Schrieffer (BCS) theory¹ or its extensions.² However, the number of superconductors that cannot be fully understood within the framework of phonon-mediated-pairing is growing. In the so-called unconventional superconductors, some unique properties of the materials have been suggested to be closely related to the novel mechanism of electron pairing. For example, studies have suggested that superconductivity in cuprates³ and iron-based compounds⁴ may be closely related to the magnetic properties of these systems while the unconventional electron pairing in heavy fermion superconductors may be associated with the enhanced electron mass in the materials. Another interesting aspect is the relation between the anisotropic electronic structure and the pairing mechanism in some unconventional superconductors such as layered cuprates,³ iron-based superconductors,⁴ and quasi-one-dimensional (Q1D) organic superconductors.⁵ Because of the low-dimensionality of the crystal structure and the anisotropic normal-state Fermi surface, it is not surprising that some properties of the superconductors, such as critical field, penetration depth, etc. are also found to be strongly anisotropic. However, from a more fundamental point of view, whether there is an intrinsic correlation between an anisotropic crystal structure and a novel pairing mechanism in low-dimensional materials has not been well understood.

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Recently, superconductivity has been observed in a number of inorganic chalcogenides including $\text{Nb}_2\text{Pd}_x\text{Se}_5$,⁶ $\text{Nb}_2\text{Pd}_x\text{S}_5$,^{7,8} $\text{Ta}_2\text{Pd}_x\text{S}_5$,⁹ $\text{Nb}_3\text{Pd}_x\text{Se}_7$,¹⁰ and $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$.¹¹ Single crystals of these chalcogenide superconductors are all needle-like with a preferred growth direction along the b -axis of the monoclinic crystal structure. Theoretical calculations on some Q1D chalcogenide superconductors^{6,10} have suggested that the Fermi surface in the normal state of the materials is strongly anisotropic and consists of multiple bands. In the superconducting state, chalcogenide superconductors are all found to have an extremely large upper critical field (H_{C2}), which is strongly anisotropic and well above the BCS Pauli limit^{6–11} similar to Q1D organic superconductors. In addition, electron transport measurements on these materials have showed an unusual insulator-like or a semiconductor-like temperature coefficient in the resistivity curve in a temperature range right above the T_C , reminiscent of the transport behavior of an underdoped cuprate superconductor in the pseudogap phase.¹² Because low-dimensionality, multi-band Fermi surface, extremely high and anisotropic upper critical field, and unusual non-metallic transport characteristics are all often regarded as key signatures for emergence of unconventional superconductivity, the above observations on chalcogenide superconductors might also be suggestive of existence of an unconventional type of superconductivity in these materials.

As one of the most important aspects in superconductivity, the order parameter (i.e. energy gap) has often been investigated to develop the understanding of the electron pairing mechanism. For the Q1D chalcogenide superconductors, several experiments have been performed to investigate the order parameter symmetry to date. Specifically, thermal conductivity measurements on $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$ indicate a non-vanishing κ/T coefficient as temperature approaches zero, implying the existence of a finite quasiparticle density.¹¹ A residual quasiparticle density at zero temperature in the superconducting state suggests the presence of nodes in the energy gap. In contrast, a transverse-field muon spin relaxation (μSR) study on Nb_2PdS_5 single crystals indicates that the superfluid density becomes practically temperature independent below 2 K, which is consistent with a fully gapped scenario.¹³ In the present study, we used point contact Andreev reflection spectroscopy to probe the order parameter of $\text{Nb}_2\text{Pd}_x\text{Se}_5$. Our results clearly indicate that the superconductor has a double-gap structure and the amplitudes of both order parameters show angular dependence in the a - c plane of the crystal structure. In addition, a large gap to T_C ratio obtained based on a modified BTK model is strongly indicative of the existence of an unconventional pairing mechanism in the Q1D chalcogenide superconductor.

Andreev reflection spectroscopy is a versatile tool for studying the properties of various materials in the field of condensed matter physics. In particular, the method has been widely used to study the order parameter in superconductors.^{14–18} A superconductor is typically placed against a normal metal to form a point contact junction. In such a junction, each single electron in the normal metal always needs to be paired up in order to enter the energy gap of the superconductor. As a result, a hole with an opposite spin will be generated at the interface and bounce back into the normal metal so that the spin, the charge, and the momentum are conserved.¹⁹ Due to Andreev reflection, there is a Cooper pair passing through the interface for each incident electron, and thus the conductance is doubled when the bias voltage is less than or equal to the size of the gap. The conductance spectrum (i.e. dI/dV vs. bias voltage) therefore provides a direct measure for the size of the energy gap and reflects the ratio of the density of Cooper pairs to the density of quasiparticles in the superconductor.

$\text{Nb}_2\text{Pd}_x\text{Se}_5$ single crystals used in the present study were grown by either a flux method as described in Ref. 6 or chemical vapor transport (CVT). For CVT, powder of polycrystalline $\text{Nb}_2\text{Pd}_x\text{Se}_5$ was mixed with an appropriate amount of SeCl_4 as a transport agent and sealed in an evacuated quartz tube. The quartz tube was then maintained at a temperature gradient of 800 °C to 630 °C for 15 days. Needle like single crystals were harvested from the cooler end of the quartz tube. Both the flux method and the CVT method produced samples with almost the same transition temperature of around 5 K. To increase the superconducting volume fraction in the crystal, we also performed a subsequent annealing process in an Ar atmosphere (1/3 atm; filled at room temperature) at a temperature of 750 °C for 5 days. The superconducting transition temperatures were consistently found to be nearly the same for as-grown and annealed single crystals while the annealed samples displayed sharper superconductor transitions. In addition, the conductance spectra

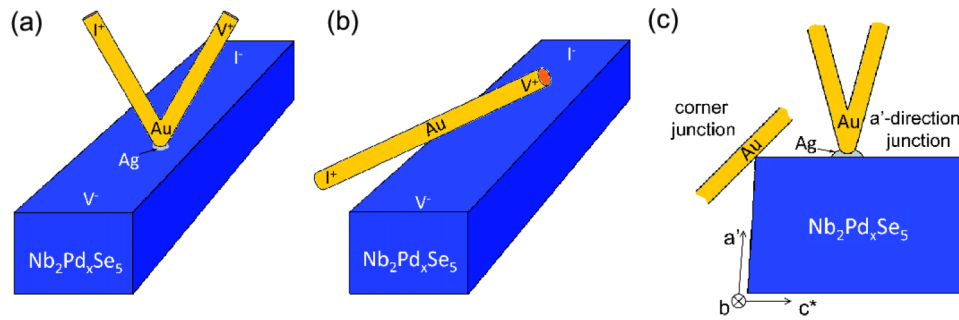


FIG. 1. Schematic illustration of the two junction configurations fabricated in this study between a $\text{Nb}_2\text{Pd}_x\text{Se}_5$ single crystal and a normal metal: a) a soft-point-contact a' -direction junction ($\text{Ag}/\text{Nb}_2\text{Pd}_x\text{Se}_5$) made by contacting a pristine surface of a $\text{Nb}_2\text{Pd}_x\text{Se}_5$ single crystal using silver paint which is electrically connected to a gold wire; b) a wire-pressed corner junction ($\text{Au}/\text{Nb}_2\text{Pd}_x\text{Se}_5$) made by gently pushing a bare gold wire to an edge of a $\text{Nb}_2\text{Pd}_x\text{Se}_5$ single crystal; c) schematic cross-section views of the two junction configurations. The single crystals of $\text{Nb}_2\text{Pd}_x\text{Se}_5$ have a monoclinic crystal structure with $\beta = 101.63^\circ$ [Ref. 6]. During the growth, $\text{Nb}_2\text{Pd}_x\text{Se}_5$ single crystals form self-cleaved surfaces along the $(-2\ 0\ 1)$ and the $(1\ 0\ 2)$ planes. As described in the main text, the $[-2\ 0\ 1]$ and the $[1\ 0\ 2]$ directions are denoted as a' -direction and c^* -direction, respectively. The angle between a' -direction and c^* -direction is 87.81° .

obtained on annealed single crystals were found to show qualitatively the same characteristics as those obtained on as-grown samples.

As shown in FIG. 1, junctions between a normal metal and a single crystal of $\text{Nb}_2\text{Pd}_x\text{Se}_5$ have been fabricated in either a soft-point-contact configuration (FIG. 1(a)) where the contact was made on one of the side surfaces of the single crystal using silver paint or a wire-pressed corner junction configuration (FIG. 1(b)) where a thin gold wire was pressed onto an edge of the single crystal to make the contact. FIG. 1(c) illustrates the schematic cross-sectional views of the two junction configurations. The single crystals of the Q1D superconductor used in this study were typically $30 \times 10 \times 500\ \mu\text{m}^3$ in size, where the long direction is along the b -axis, and the diameter of the gold wires was $25\ \mu\text{m}$.

The needle-like single crystals formed self-cleaved surfaces along the $(-2\ 0\ 1)$ and the $(1\ 0\ 2)$ planes during the growth.⁶ To be consistent with Ref. 6, where synthesis of the crystals is discussed, we define a' and c^* directions as $[-2\ 0\ 1]$ and $[1\ 0\ 2]$, respectively. Our side-surface junctions were made on one of the wider side surfaces of each single crystal which was found to be consistent with the $(-2\ 0\ 1)$ plane direction, thus we denote these side-surface junctions as a' -direction junctions. Given the values of the lattice constants,⁶ the angle between a' -direction and c^* -direction is found to be 87.81° , slightly off the normal angle. The experimental results on all the a' -direction junctions are qualitatively consistent, and the typical contact area is about several tens of micrometers. In the corner junction configuration, the normal direction of the junction interface has an angle with respect to either the $(-2\ 0\ 1)$ plane or the $(1\ 0\ 2)$ plane, and the dimension of the contact area is comparable to the diameter of the gold wire. The observed junction conductance spectra together with the nominal contact areas suggest the junctions formed in the present study are in the diffusive regime and are presumably comprised of multiple paths.

Despite no definitive proof for a precise control of the direction that the current flows in each of the junctions, the directions of the current flow in the two junction configurations are presumably different. Specifically, the current in the a' -direction junction is expected to predominantly flow along a direction parallel to the a' -direction, while the current in the corner junction is expected to have an angle with either the a' -direction or the c^* -direction. As such, the two junction configurations are expected to provide directional information about the superconducting order parameter of $\text{Nb}_2\text{Pd}_x\text{Se}_5$ in the a - c plane of the crystal structure.

Using a phase-sensitive detection method, the zero bias junction resistance was typically measured to be in a range of 20-30 Ohms at low temperatures. For about 20 junctions we fabricated in either configuration, the conductance spectra at low temperatures consistently showed a typical double-gap feature (FIG. 2). However, the sizes of the two gaps measured on junctions in the two configurations were found to be quite different.

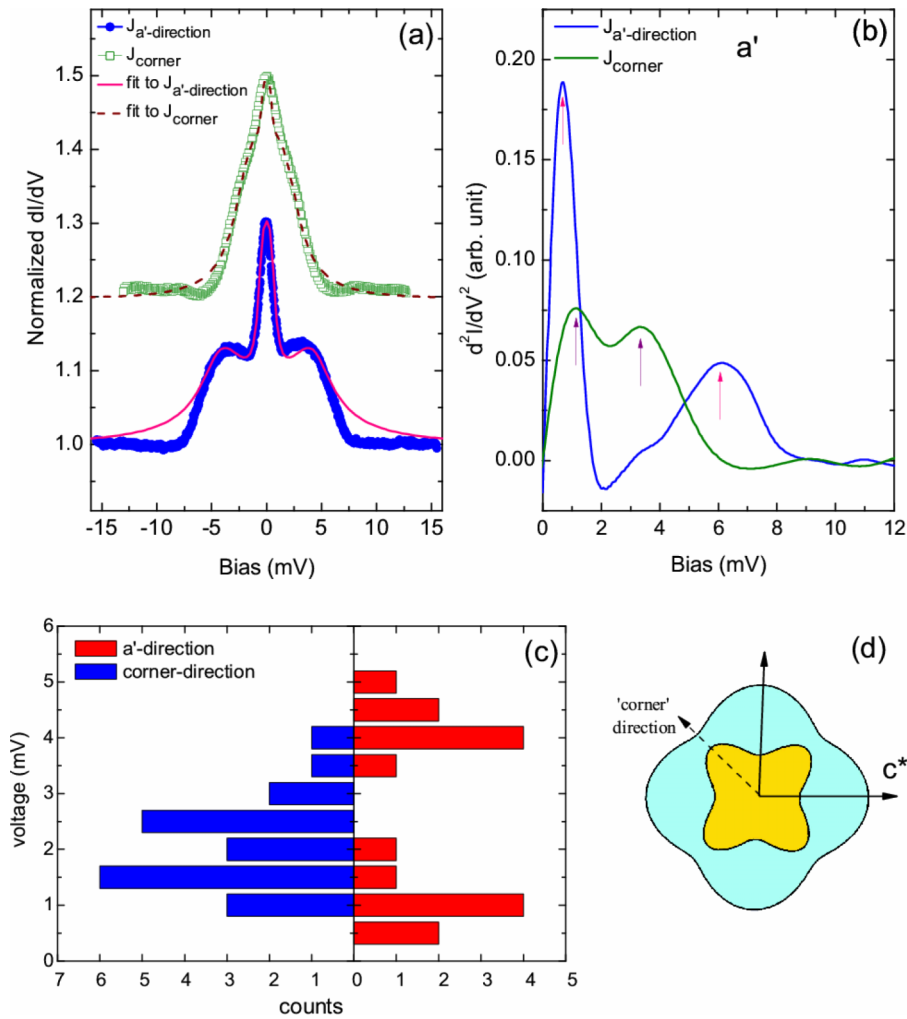


FIG. 2. a) Filled circles and open squares are two representative conductance spectra obtained at 1.8 K on an a' -direction junction and a corner junction, respectively. The solid curve and the dashed curve are the best fits to the experimental data based on a double-band BTK model as described in the text. The fitting parameters for the spectrum of the a' -direction junction are $\Delta_1 = 0.6$ meV, $\gamma_1 = 1.3$ meV, $Z_1 = 0.2$, $\Delta_2 = 4.7$ meV, $\gamma_2 = 1.5$ meV, $Z_2 = 0.4$, and the weight factor is $W_1 = 1 - W_2 = 0.62$. The fitting parameters for the spectrum of the corner junction are $\Delta_1 = 1.3$ meV, $\gamma_1 = 1.5$ meV, $Z_1 = 0.28$, $\Delta_2 = 2.3$ meV, $\gamma_2 = 1.1$ meV, $Z_2 = 0.23$, and the weight factor is $W_1 = 1 - W_2 = 0.40$. Data for the corner junction are vertically shifted up for clarity; b) Derivative of the conductance spectrum for each junction clearly shows two peaks with the bias voltage of each peak presumably corresponding to a superconductor energy gap; c) Histograms of the obtained gap values for both junction configurations; d) A schematic diagram of two anisotropic superconducting order parameters consistent with the results obtained in this study.

FIG. 2(a) shows two representative conductance spectra obtained at 1.8 K, one for an a' -direction junction and the other for a corner junction. Both curves have been normalized by a corresponding conductance spectrum measured at a temperature slightly above the T_C of the single crystal used. As shown in FIG. 2(a), both conductance spectra of the junctions show a peak at zero bias and the derivative of each spectrum (FIG. 2(b)) unambiguously indicates a double-peak feature as the bias voltage is ramped up from zero, suggesting the presence of two energy gaps in the electron density of states of the superconductor. As indicated by the arrows in FIG. 2(b), the derivative curve for the a' -direction junction shows two peaks at 0.7 mV and 6.2 mV, while the derivative curve for the corner junction shows two peaks at 1.1 mV and 3.3 mV. The positions of the peaks provide estimates for the corresponding superconducting energy gaps. It is known that the phonon peaks of Au can sometimes appear at ≈ 9 mV and ≈ 16 mV, while the phonon peaks of Ag

can appear at ≈ 12 mV and ≈ 20 mV²⁰; based on the observed peak positions, we rule out phonons as the origins of the peaks.

To quantitatively describe the entire conductance spectra of the junctions, a modified double-gap Blonder-Tinkham-Klapwijk (BTK) model^{21,22} is applied. Specifically, in the modified double-gap model, it is assumed that the overall conductance spectrum is a sum of two linearly-weighted Andreev reflection spectra corresponding to the two superconducting energy gaps. As indicated by the solid curves in FIG. 2(a), both spectra can be described by the model with a spectrum broadening term γ , resulting in a pair of energy gaps of 0.6 meV and 4.7 meV, and of 1.3 meV and 2.3 meV for the a' -direction junction and the corner junction, respectively. The values are qualitatively consistent with these estimated from the derivative of the conductance spectra (FIG. 2(b)). The results suggest that the amplitudes of the order parameters obtained in the two junction configurations may not be the same even after a measurement uncertainty is considered. FIG. 2(c) shows histograms of the gap values obtained from conductance spectra of the junctions in both configurations. Quantitative analyses based on the distribution of the obtained gap values consistently yield a larger difference between the two gap values for a' -direction junctions than that for corner junctions.

In the BTK model, the dimensionless parameter Z is introduced to describe the interfacial scattering strength. It takes both the physical barrier and band structure effects such as Fermi velocity and effective mass mismatches into account. In the present study, Z values associated with the two superconducting gaps were always found to be relatively small, suggesting that Andreev reflection is the dominant effect at the interfaces of these junctions. Moreover, the slight difference in the obtained Z values for each conductance spectrum may suggest that the degrees of mismatch in Fermi velocity or effective mass for the two distinct superconducting bands may be different. Another interesting aspect we noticed in our quantitative analysis is that in some cases, the inelastic broadening term γ appears to exceed the superconducting energy gap value. As discussed in the following section, we propose that the obtained large γ term in applying the BTK model may be indicating an averaging effect of an anisotropic superconducting energy gap in the present case.

As mentioned previously, the current in a' -direction junctions is expected to overwhelmingly flow along a direction parallel to the a' -direction (FIG. 1(a)); however, the current flow direction in corner junctions may have an angle to both the a' -direction and the c^* -direction. Therefore, the different sizes of the energy gaps obtained on the two junction configurations may reflect an intrinsic anisotropic property of the order parameters of the Q1D material.

FIG. 2(d) shows a schematic illustration of two anisotropic superconductor order parameters in the a - c plane of the crystal structure consistent with the results of the present study. In fact, because of the monoclinic crystal structure and the anisotropic multi-band fermi surface in the normal state,⁶ it is perhaps not unreasonable that there are two anisotropic order parameters in this chalcogenide Q1D superconductor. However, because of the size of our junction areas, there is a finite spread in the direction of the current flow. Thus, we are far from being able to obtain a fully angle-resolved picture of the order parameters in the a - c plane. In addition, we also expect that the spread in the current flow direction at the junction interface likely results in an averaging effect of the conductance spectrum, making the feature of the energy gap less sharp as compared to that in junctions with isotropic s-wave superconductors. Therefore, the averaging of the order parameters in a range of angles may induce a relatively large broadening term γ ²² in the modified BTK model which is used to fit the spectra. In our measurements, a broadening term with a typical value of ~ 1.0 - 1.5 meV was consistently obtained by applying the modified BTK model. In this model, the γ term was originally introduced to empirically describe spectrum broadening due to inelastic scattering or pair breaking effect.²² The results of the present study suggest that such an empirical term γ may also be able to describe directional averaging effect of an anisotropic order parameter despite a somewhat unusually large value obtained from the BTK model. An improved model with a complete physical explanation may be required to further understand the averaging effect in directional Andreev reflection measurements on a superconductor with an anisotropic order parameter.

We note that similar zero bias peak in the conductance spectrum has been reported as a signature of d -wave superconductivity in many superconductors including cuprates^{23,24} and PuCoGa_5 .²⁵ In such studies, the zero-bias peak is regarded as evidence for a finite quasiparticle density of states

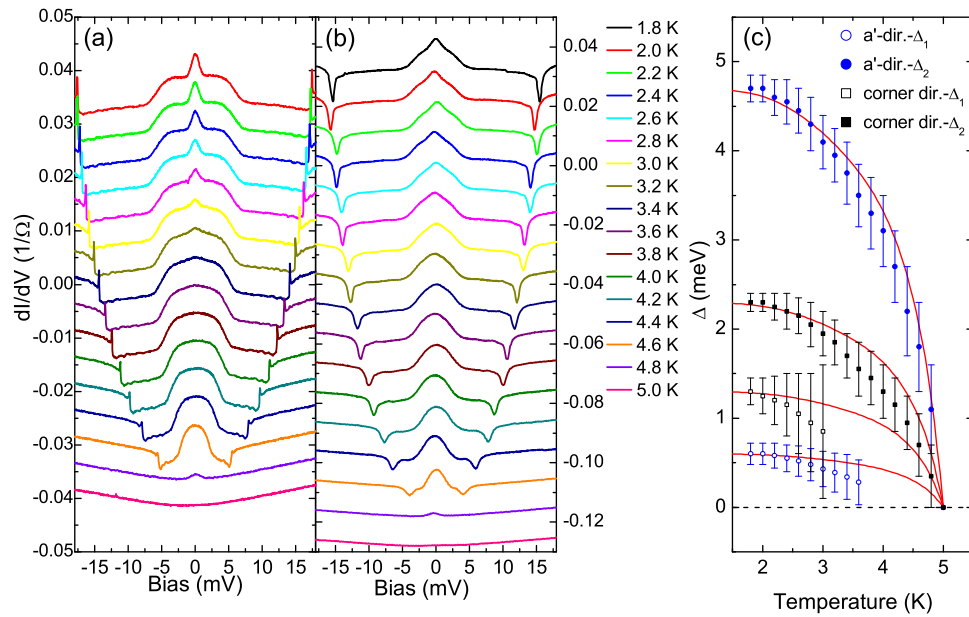


FIG. 3. a) and b) Conductance spectra obtained at different temperatures for a a' -direction junction and a corner junction, respectively. On each plot, the curves are vertically shifted for clarity except the one at 1.8 K. c) Temperature dependence of the superconductor energy gaps obtained for both junctions. Red curves in the plot show the temperature dependence of energy gap consistent with the BCS theory.

near the nodes. To verify whether the d -wave scenario could explain the experimental data in the present study, we have attempted to use the model developed in Ref. 25 to describe the obtained conductance spectra. This, however, did not yield satisfactory fitting results, suggesting that the d -wave model does not apply to the Q1D superconductor.

FIG. 3(a) and FIG. 3(b) show the temperature dependence of the conductance spectrum from an a' -direction junction and a corner junction, respectively. For both junctions, the double-gap feature gradually disappears as temperature increases. An interruption at a high bias voltage in the conductance spectrum is generally observed in our measurements. This above-gap feature moves to lower bias voltages as temperature increases and eventually disappears at the superconducting transition temperature of the Q1D single crystal. Such an above-gap conductance discontinuity has been attributed to loss of interface superconductivity due transport current exceeding the critical current density in the junction area.²⁶ Therefore, we believe that the feature at such a high bias is not associated with superconducting energy gap.

The enhanced feature corresponding to the smaller superconductor gap in both configurations seems to vanish at a temperature much lower than the T_C of the single crystal. However, such a transition from a clear double-gap spectrum to a single-gap-like spectrum does not necessarily suggest that the corresponding superconducting energy gap closes up at a temperature below the T_C . Similar single-gap like spectrum at a moderate temperature below T_C has also been observed in Andreev reflection junctions fabricated on other double-band superconductors such as MgB_2 ¹⁶ and iron-based superconductors.²⁷ In such previous studies, the feature corresponding to the smaller superconducting gap in conductance spectrum is presumably smeared out by a spectrum broadening effect as the temperature is increased. In the case of $\text{Nb}_2\text{Pd}_x\text{Se}_5$, aside from the spectrum broadening effect, the likely averaging effect of the anisotropic order parameter in the a - c plane may also play a role in the broadened Andreev reflection enhancement, thus making one of the gap features in the conductance spectrum undistinguishable even at temperatures slightly below the T_C .

FIG. 3(c) shows the temperature dependence of the gap values determined from quantitative fits to the conductance spectra of both types of junctions using the modified BTK model. The red curves in the plot are fits to the BCS theory. Within an experimental error, the reduced temperature dependence of the larger gap agrees well with that of a BCS type superconductor gap. However,

a large uncertainty in determining the value of the smaller gap prevents its further quantitative analysis.

According to the gap values obtained from the two representative conductance spectra, the $2\Delta/k_B T_C$ ratios are ~ 2.8 and ~ 21.8 for the a' -direction junctions, while they are ~ 6.0 and ~ 10.7 for the corner junctions. Compared to the BCS weak coupling limit for an isotropic s -wave superconductor, the $2\Delta/k_B T_C$ ratio of the smaller gap seems to swing from a small value to a relatively large one within the a - c plane. On the other hand, the ratio corresponding to the larger gap is much larger than the BCS weak coupling value of 3.53 for phonon-mediated pairing. To the best of our knowledge, a $2\Delta/k_B T_C$ ratio greater than 20 has only been previously reported in the heavy fermion superconductor CeCoIn_5 .²⁸ In CeCoIn_5 , the large gap-to- T_C ratio is attributed to an enhancement through interband coupling and is regarded as a signature of an unconventional pairing mechanism in the heavy fermion superconductor. In the case of $\text{Nb}_2\text{Pd}_x\text{Se}_5$, given the fact that the material has a complex fermi surface consisting of three electron and hole bands,⁶ the pairing of electrons between different bands may also follow an unconventional mechanism, thus resulting in a substantially enhanced gap. We believe that the extremely large gap-to- T_C ratio obtained in our Andreev reflection measurements provides an indirect evidence for the unconventional pairing mechanism in the anisotropic multi-band Q1D superconductor. However, to establish a definitive picture of the pairing mechanism in the superconductor, further theoretical and experimental studies are needed.

FIG. 4(a) shows a field evolution of the conductance spectrum obtained on the a' -direction junction at 1.8 K. The external magnetic field was applied along the direction perpendicular to the junction interface. The Andreev reflection enhancement in the conductance spectrum is still clearly present at 9 Tesla, suggesting that the single crystal used in the junction remains superconducting at 9 Tesla, which is consistent with the previous electronic transport results.⁶

In a previous study on a single gap superconductor, the energy gap obtained by applying the modified BTK model to spectra at different magnetic field shows linear dependence on the squared of the field, and the extrapolation of the line fit coincides with the square of the critical field.²⁹ The field dependence of the superconducting energy gap in many other single gap superconductors has also been found to follow such a quadratic relation. As a result, it has been further suggested that the observed common behavior may be indicative of the existence of an additional anisotropy axis

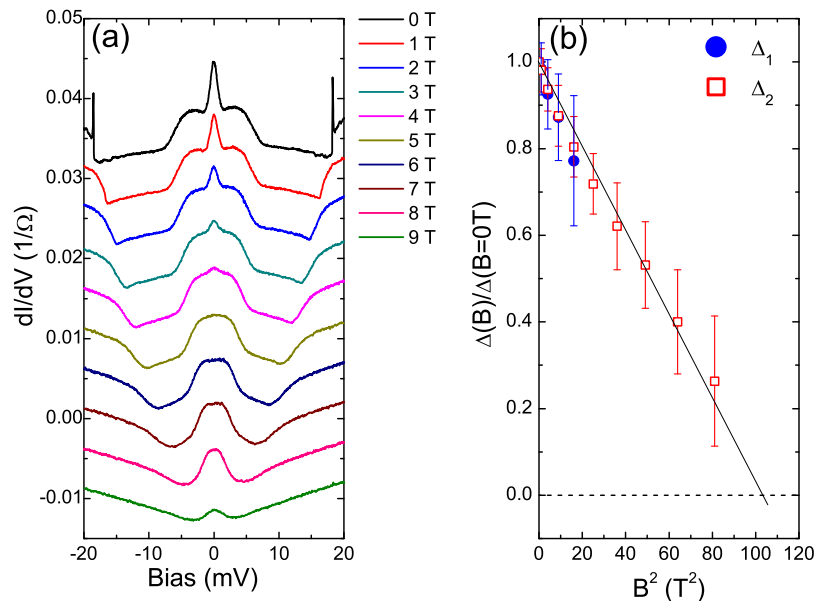


FIG. 4. a) conductance spectra of an a' -direction junction obtained at different fields. The curves are shifted downward except the one at zero field for clarity; b) Normalized superconductor energy gap values obtained by applying the modified BTK model are plotted as a function of square of the magnetic field for both gaps. The line represents B^2 dependence of the reduced superconducting energy gap.

that breaks the intrinsic symmetry in the systems.²⁹ In FIG. 4(b), we plot the reduced gap size as a function of the square of the field for both superconducting gaps obtained on Nb₂Pd_xSe₅. Clearly, the larger superconducting gap is in good agreement with the proposed B² dependence, and the extrapolation suggests an upper critical field of ~10.2 Tesla for the direction. In addition, despite of a large uncertainty of the gap value, the smaller gap seems to also follow such a trend. The results strongly suggest that the pair-breaking model proposed in Ref. 29 may also at work in the Q1D chalcogenide superconductor. However, the exact nature of the symmetry breaking ordering in Nb₂Pd_xSe₅ still needs to be examined in the future.

In summary, we have systematically studied the superconducting order parameter of the Q1D chalcogenide superconductor Nb₂Pd_xSe₅ using Andreev reflection spectroscopy. A clear double-gap feature was consistently observed in junctions between a Nb₂Pd_xSe₅ single crystal and a normal metal. A directional study realized by fabricating contacts in a'-direction junctions and corner junctions suggests that the two order parameters in the superconductor are anisotropic. A large gap-to-T_C ratio obtained from the conductance spectroscopy is suggestive of the presence of an unusual pairing mechanism in the Q1D multi-band superconductor.

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