

論文の内容の要旨

論文題目 Gate-induced Superconductivity and Nonreciprocal Transport
in Chiral Nanotubes
(カイラルナノチューブにおける電界誘起超伝導と非相反
輸送現象)

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1. Introduction and motivation

Scaling down the dimensionality of system is always interesting in the research field of condensed matter physics, due to various fascinating phases emerging from competition between condensations and fluctuations. For instance, superconductivity, the most famous condensed phase in materials, shows totally different behaviors when scaling down the system dimensions and finally disappears in one dimension due to strong quantum fluctuations. Therefore, recently Two Dimensional (2D) superconductors in atomically thin metals, mechanically exfoliated 2D materials, and various hetero interfaces attracts lots of interest.

Beyond those 2D materials, nanotube (NT) should be a new platform for the nanoscaled superconductor because of its unique geometry with intermediate dimension. Moreover, NT has a distinct topology compared with usual materials, indicating novel properties originating from quantum interference along the NT circumference. The relations between geometry of materials and superconductivity are highly anticipated to yield unexpected quantum phenomena. Hence, the superconducting NT, once realized, will be a potential material for searching exotic phenomena and nontrivial superconductivity due to its uniqueness in geometry,.

So far the superconductivity in NTs has not been well-studied because of the lack of suitable materials. Although there are intensive studies of superconductivity in carbon NTs in the past years, those researches have only investigated properties of superconductivity in the assembled form of NTs. Until now the superconducting properties reflecting the unique geometry, such as curvature and chirality of individual NT, have remained elusive.

Above all, we are focusing on another NT made of tungsten disulfide (WS_2) based on three reasons. First, WS_2 NT is famous and well-characterized, because it is the first inorganic NT synthesized in 1992, just one year after the birth of carbon NT. Second, WS_2 is a member of Transition Metal Dichalcogenides (TMDs) family which is thought to be now 2D materials beyond graphene. Recently TMD materials are now attracting significant attention because of novel properties and prospective applications for electronics, photonics, spin-tronics, mechanics, as well as valley-tronics. Third, recent systematic studies have clarified that a lot of TMDs, including WS_2 , are semiconductors without carrier doping, exhibit superconductivity under the ionic liquid gating technique. Hence, WS_2 NT is a promising candidate to realize superconductivity with novel properties and broad applications in the future.

Thus, in this study, we have measured the transport properties of individual WS_2 NT under ionic liquid gating. From the perspective of material science, we aim to realize superconductivity in individual WS_2 NTs, and from the perspective of physics, we aim to clarify the novel properties arising from its peculiar tubular and chiral structure of WS_2 NTs.

2. Experiment and sample characterization

In recent experimental advances, by replacing the solid dielectric with polymer electrolyte or ionic gel/liquid, a new type of Field Effect Transistor (FET), so called Electrical Double Layer Transistor (EDLT), has been demonstrated to have the capability to accumulate over ten times higher carrier density ($> 10^{14} \text{ cm}^{-2}$) even at low gate bias voltages, compare to the conventional solid gate FET. Such ionic liquid gating technique is a powerful technique to realize electrostatics doping onto the surface of sample, and thus manipulate electronic properties of sample. Very recently, a new gate-induced electronic modulation technique has been realized and systematically studied. Beyond electrostatic carrier doping, it realizes electrochemical doping induced by ionic liquid gating, which is demonstrated that the positive ions diffuse into the interlayer of the bulk materials and realizing extremely high carrier doping not onto the surface but into the whole bulk.

We have performed transmission electron microscope image of a single WS₂ NT, the tube have multi-wall structure with an outer diameter ranging from tens to hundreds nanometers. According to the literature, the tube part has a 2H-polymorph-layered structure of WS₂, where each tungsten atom is surrounded by six sulfur atoms in a trigonal biprism coordination (space group P6₃/mmc). From the electron diffraction pattern of a single WS₂ NT, most of tubes contain multi-type chirality.

3. Gate-induced superconductivity in individual nanotubes

The carrier density of WS₂ NT was successfully tuned by liquid gate technique, and a repeatable and reversible ambipolar transfer curve with a high on/off ratio ($>10^2$) was observed for both hole and electron sides. In addition to the electrostatic doping in EDL region, the electrochemical doping was realized. During the intercalation process, the source drain current increased more than two orders difference and the intercalated WS₂ NTs displayed well-metallic properties and thus performed superconductivity in low temperature. This is the first observation of superconductivity in individual NTs.

The anisotropic superconducting properties in individual WS₂ NT were observed. The superconductivity rapidly disappeared with increasing the external magnetic field perpendicular to the NT axis, while the superconductivity was robust against the external magnetic field in the parallel case to the tube axis. The anisotropic superconductivity was also confirmed by angular dependence and temperature dependence of the upper critical field. Besides anisotropic properties of superconductivity, the possible staging phase and nontrivial pairing mechanism is discussed. This result encourages researchers to explore new superconductors by ionic liquid gating, and offers them a great opportunity to investigate exotic properties originating from a peculiar structure.

4. Little-Parks oscillations and diameter-dependent of T_c

When the external magnetic field was applied parallel to the tube axis, the magnetoresistance at various temperatures have shown the periodic oscillation during the superconducting transition, known as Little-Parks effect, originating from the quantum interference of the supercurrent along the circumference of NT and thus resultant oscillation of critical temperature, from which the diameter of certain NT was estimated. This result provides solid evidence that the superconductivity occurs in the nanoscaled cylindrical structure, and attracts a great of interest in the superconducting NT.

Thus the first systematic study of diameter-dependent of superconductivity was discussed by summarizing multiple observation of superconductivity in multiple tubes with different diameters. The critical temperature (T_c) of superconductivity decreases linearly as a function of the inverse diameter of the nanotube, which implies that the superconductivity is affected by the tube diameter, that is, curvature effect of the nanotube. By carefully ruling out other possibilities affecting T_c such as carrier density or wall thickness, the observed systematic relation is consequently considered as purely curvature effect of the nanotube. The present results provide crucial information for understanding the microscopic mechanism of superconductivity in an individual nanotube.

5. Chirality and nonlinear transport properties

This is the first experimental discovery that is demonstrated on the nonreciprocity of superconductivity. An unambiguous evidence of the superconductivity reflecting chiral structure of NT was observed, in which the forward and backward supercurrent flows were not equivalent because of inversion symmetry breaking. The observed nonreciprocal signal was significantly enhanced within the superconducting state due to the highly coherence nature of superconductivity, and became negligibly small in the normal state. In addition, the nonreciprocal signal was associated with unprecedented quantum Little-Parks oscillation. Furthermore, it was interesting that the nonreciprocal signal displayed stepwise behavior at low temperature, affected by the flux quanta passing through the tube. The current results inspire researchers to further pursue the research on the microscopic mechanism of nonreciprocity of superconductivity and pairing symmetry in chiral or noncentrosymmetric structure.

6. Summary

In this study, basic superconducting properties of individual WS_2 NT are investigated. The study demonstrates of high performance of field effect on individual WS_2 NT by liquid gating technique, and discovers of a new type superconducting material. For the knowledge of basic physics, both the curvature effect and chirality effect on the superconductivity have been revealed for the first time. In the view of wealthy family of materials, this study implies the TMD NT should be a new platform for the researches on nanoscaled devices beyond 2D TMD materials and carbon NT.