Letter

Spontaneous voltage peaks in superconducting Nb channels without engineered asymmetry

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Rectification effects in solid-state devices are a consequence of nonreciprocal transport properties. This phenomenon is usually observed in systems with broken inversion symmetry. In most instances, nonreciprocal transport arises in the presence of an applied magnetic field and the rectified signal has an antisymmetric dependence on the field. We have observed rectification of environmental electromagnetic fluctuations in plain Nb channels without any asymmetry in design, leading to spontaneous voltage peaks at the superconducting transition. The signal is symmetric in the magnetic field and appears even without an applied field at the critical temperature. This is indicative of an unconventional mechanism of nonreciprocal transport resulting from a spontaneous breaking of inversion symmetry.

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Nonreciprocal transport is observed in conductors lacking inversion symmetry. Two prominent experimental signatures of this phenomenon are the rectification of a.c. signals into a dc voltage and the generation of even harmonic frequencies. In most cases, nonreciprocal transport occurs in the presence of an applied magnetic field. It has been observed in a variety of superconducting devices. Some examples are noncentrosymmetric superconductors [1,2], polar superconductors with Rashba-type spin-orbit interaction [3], topological insulator/superconductor interfaces [4], and amorphous superconductors attached to a magnetic material [5]. Rectification effects in asymmetric ratchet devices [6–8] have been widely studied. The superconducting diode effect, which is characterized by a difference of critical currents for two opposite bias polarities, is currently a very active area of research [9–12]. In this work, we report the observation of spontaneous voltage peaks in plain channels of superconducting Nb which demonstrates that nonreciprocal transport is possible even in the absence of an asymmetry in the physical structure of the system. The fundamentally different origin of this unconventional mechanism will be discussed on the basis of the symmetry properties of the rectification signal as a function of the applied magnetic field.

The resistance (R) of a system exhibiting nonreciprocal transport, as a function of current (I), may be expressed as $R = R_0 + \alpha I$, where R_0 is the resistance in the limit of zero current and α is the parameter describing the nonreciprocity in transport. Application of an a.c. current at frequency f with r.m.s. amplitude $I_{\rm ac}$ results in a r.m.s. voltage $V_{2f} = \frac{1}{\sqrt{2}}\alpha I_{\rm ac}^2$ at the second harmonic frequency $2f$ as well as a dc voltage $V_{dc} = \frac{1}{\sqrt{2}}\alpha I_{\rm ac}^2$ (see the Supplemental Material [13] for the derivation). The relationship between geometrical asymmetry and nonreciprocal transport can be understood within the framework developed by Rikken *et al.* [14] for magnetochiral anisotropy. General arguments regarding the implications of time-reversal symmetry on two-terminal resistance show that a nonreciprocal signal must be antisymmetric with respect to the magnetic field. In such cases, α has the form γB, where γ describes the asymmetry inherent in the structure of the system and B is the magnetic field. These results apply across a wide class of systems, irrespective of the microscopic mechanism involved. Accordingly, the observation of nonreciprocal transport usually requires both the breaking of inversion and time reversal symmetries, with the quantity characterizing this phenomenon [15] having an antisymmetric dependence on the magnetic field [1–5,9,12,16–20].

Our experiments were conducted on superconducting channels of Nb realized on commercially available Si wafers coated with 500 nm of SiO_2. The devices were patterned using electron beam lithography, following which we evaporated a layer of Nb (thickness between 55 nm to 72 nm). The superconducting critical temperature (T_c) of the samples varied from one batch to another. The T_c of niobium depends strongly on the quality of vacuum in the deposition chamber [21] and average grain size [22]. Further, contamination from electron beam resist contributes to a significantly lower T_c of narrow channels with widths below a few micrometres. We were thus able to study superconducting devices with varying degrees of disorder and a wide range of critical temperatures (2.5 K–7.7 K). Electrical contacts were established with ultrasonic wirebonding directly on contact pads of the sample. The electrical lines inside the cryostat used for transport measurements have a resistance of about 1 Ω each, measured from the external connectors at room temperature down to the sample stage.

Figure 1(a) shows the schematic diagram of a sample named D1. It consists of a channel of width (w) 38 µm and length (L) 245 µm, connected to two large contact pads. The

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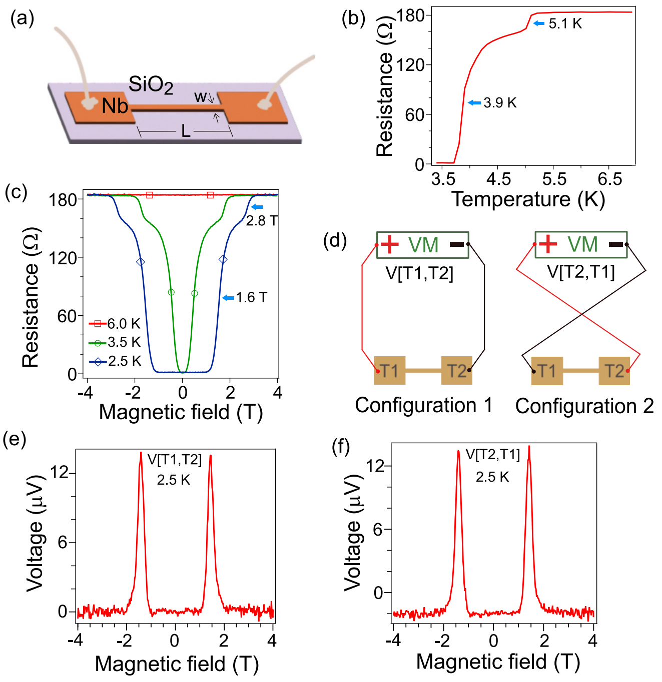

FIG. 1. (a) Representation of the geometry of sample D1. (b), (c) Observation of the superconducting transition by measuring the resistance as a function of temperature (b) and magnetic field (c). The dc current applied was 1 µA. (d) Schematic diagram of the measurement of voltage across the sample without any applied bias current using a dc voltmeter (VM). (e) Spontaneous voltage peaks as a function of magnetic field with the circuit of configuration 1. (f) Spontaneous voltage peaks as a function of magnetic field with the circuit of configuration 2.

thickness of the Nb film is 72 nm (see the Supplemental Material [13] for images). The variation of resistance measured in a two-probe configuration with temperature (T) is shown in Fig. 1(b). We determine T_c and the upper critical magnetic field (B_{c2}) by the midpoint of the resistance drop. For magnetoresistance measurements, the magnetic field was applied perpendicular to the plane of the sample.

There are two superconducting transitions in Fig. 1(b), corresponding to the critical temperatures of the large pads (5.1 K) and the central channel (3.9 K). At a temperature of 2.5 K, we observed B_{c2} of 2.8 T for the pads and 1.6 T for the channel [Fig. 1(c)]. We will now focus on the response of the device in the absence of any applied bias current. For this, we simply connected a voltmeter across the sample [schematic diagram in Fig. 1(d)]. The contact pads are labeled T1 and T2. There are two ways of connecting the voltmeter leads across a two-terminal device (marked as configurations 1 and 2). We adopt the convention of denoting the measured voltage as V[T1,T2], where the first (second) contact is the one connected to the positive (negative) terminal of the voltmeter input. The voltmeter used was a Keithley DMM6500 Multimeter (henceforth DMM). Upon sweeping the magnetic field, we observed two sharp peaks in the measured voltage [Fig. 1(e)] almost coinciding with B_{c2} of the central channel. Such voltage peaks at the critical field transition, without an application of a dc current, have been reported in MoGe/$Y_3Fe_5O_{12}$ heterostructures [5] and $NbSe_2$ [2]. The origin of the phenomenon is that a superconducting system acts as a rectifying antenna capable of generating dc electricity from nonequilibrium environmental electromagnetic fluctuations. The voltage peaks at the critical field in our devices can be explained as a manifestation of a similar phenomenon [23]. However, there are two surprising facts which make our observation very different from the results in Refs. [2,5]. First, we observe a rectification effect even when there is no apparent source of asymmetry in the system. Second, the devices in Refs. [2,5] show antisymmetric voltage peaks understood from a mechanism of magnetochiral anisotropy, whereas we observe symmetric-in-field peaks defying common expectations. A dc voltage requires a preferential direction to determine its polarity. How this biasing happens is a key question that needs to be understood. If the polarities develop at random, an even distribution of positive and negative peaks is expected. However, in most instances, we observed positive peaks in our measurements (for reasons that will be explained later). Further crosschecks yielded unexpected results. We interchanged the leads of the voltmeter on the contact pads to measure V[T2,T1] [configuration 2 in Fig. 1(d)]. We would expect V[T2,T1] to have the opposite sign of V[T1,T2], but, upon sweeping the magnetic field, we still observed [Fig. 1(f)] positive voltage peaks. This shows that the spontaneous voltage peaks are not only related to the superconducting transition within the niobium device, but also to an influence of the internal circuitry of the voltmeter which determines the polarity. Further discussions on this issue will be presented later.

We now present results from a second sample D2 [Fig. 2(a)]. This consisted of a central channel ($w = 40$ µm) for applying a current (between contacts C1 and C2) and eight probes for measuring voltage (numbered from U1 to U8). The thickness of the Nb film was 55 nm. The voltage probes consisted of narrow channels a few micrometres wide [Fig. 2(b)], with reduced T_c (< 3.0 K). Standard four-probe measurements showed a sharp superconducting transition at 7.7 K in the central channel connecting C1 and C2 (see the Supplemental Material [13] for the characterization of sample D2). Figure 2(c) shows the result of four-probe resistance measurement using a standard lock-in technique. A current of 1 µA r.m.s. was applied between C1 and C2. The voltage was measured between probes U1 and U4 with a Stanford Research Systems SR830 lock-in amplifier. Simultaneously, a DMM measured the dc voltage between the same contacts, U1 and U4 [Fig. 2(d)]. The resistance drop at the superconducting transition at B_{c2} [Fig. 2(c)] was accompanied by dc voltage peaks [Fig. 2(d)].

An a.c. current ($I_{ac} = 5$ µA, $f = 13.27$ Hz) was applied between contacts C1 and C2 of sample D2. V_{2f} (the voltage at frequency $2f = 26.54$ Hz) was measured between probes U1 and U4. The corresponding resistance $R_{2f} = V_{2f}/I_{ac}$ is shown in Fig. 2(e). We observed sharp peaks in R_{2f} at the critical field transition. This further confirms that the superconducting transition is associated with even-in-field nonreciprocal transport properties and a finite value of the nonreciprocity parameter α.

The resistance of the conduction channel between contacts U7 and U8 was measured in a two-probe configuration

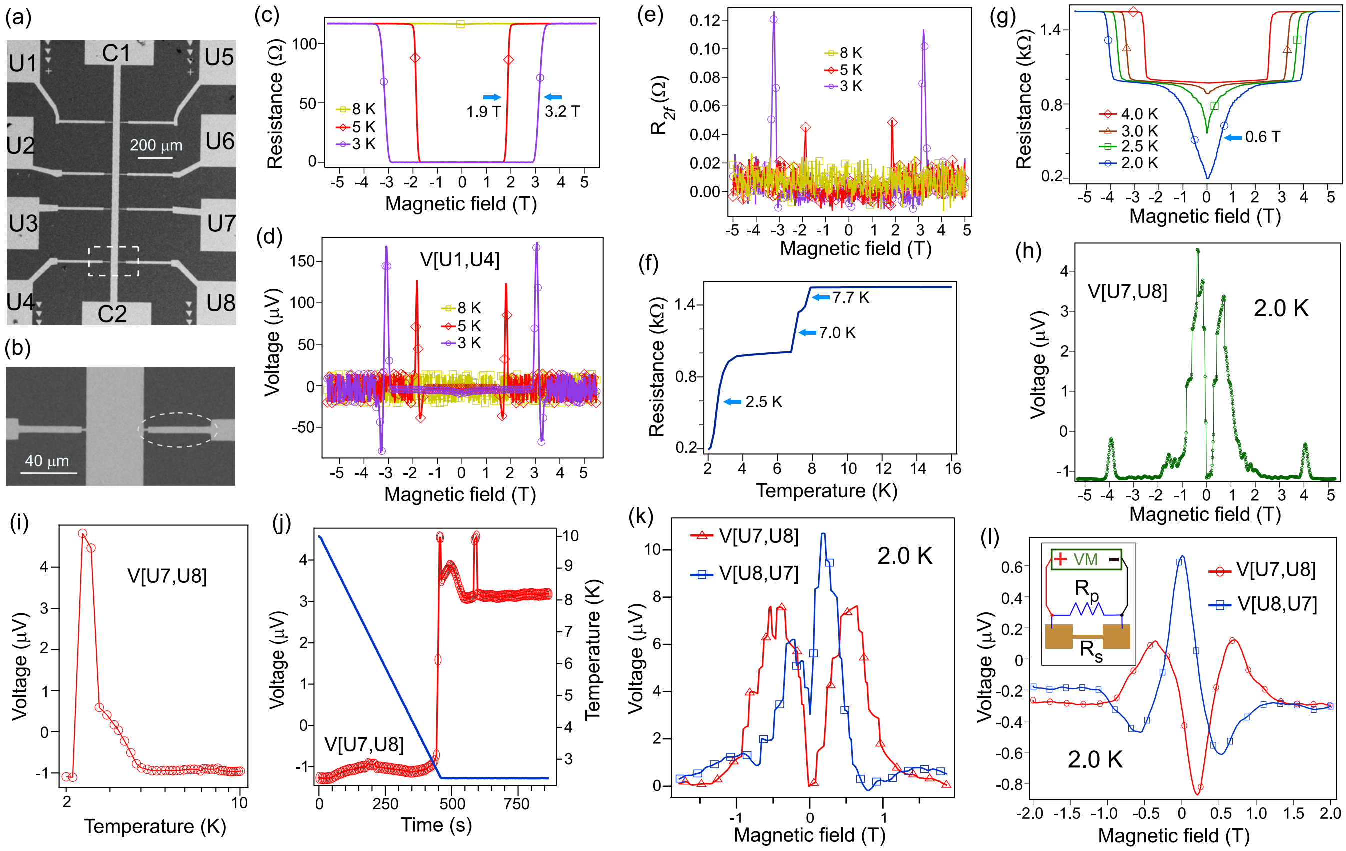

FIG. 2. (a), (b) Sample D2 observed in the scanning electron microscope (SEM). A close up of the narrow channels of the voltage probes [dashed rectangle in (a)] is shown in (b). (c) Four-probe measurement of resistance using a low frequency lock-in technique. (d) Measurement of V[U1,U4] with a DMM simultaneously with the resistance measurement described in (c). (e) R_{2f} estimated from the voltage at the second harmonic frequency measured between U1 and U4. (f), (g) Two-probe resistance measurement as a function of temperature (f) and magnetic field (g) across U7 and U8, using an applied dc current of 78 nA. (h) Measurement of V[U7,U8] without any applied bias current with a nanovoltmeter as a function of magnetic field. (i) Measurement of V[U7,U8] without any applied bias current with a nanovoltmeter as a function of temperature at zero field. (j) The spontaneously arising voltage V[U7,U8] (open circles) is measured with a variation of temperature (line). When the temperature reaches 2.4 K, it is held constant and the voltage is recorded with time. (k) Measurement of spontaneous voltage across U7 and U8 as a function of magnetic field by interchanging the polarities of nanovoltmeter leads on the two contacts. (l) Measurement of V[U7,U8] and V[U8,U7] as a function of the magnetic field. (Inset) Circuit implemented with a resistor R_p in parallel with the sample.

as a function of temperature [Fig. 2(f)]. The narrow segments [marked by a dashed ellipse in Fig. 2(b)] have a broad transition with a T_c of 2.5 K. The zero resistance state is still not reached at the lowest accessible temperature of 2.0 K. The critical magnetic field of these segments at 2.0 K was determined to be 0.6 T from resistance measurements [Fig. 2(g)]. Figure 2(h) shows the measurement of spontaneous voltage without an applied current, using a Keithley 2182A nanovoltmeter. The transitions of wide and narrow regions correspond to two voltage peaks around 4.0 T and 0.6 T, respectively. A spontaneous voltage was also seen to develop at the superconducting transition induced by varying the temperature at zero magnetic field [Fig. 2(i)]. It is therefore evident that the phenomenon of rectification is associated with both the field-induced and temperature-induced transitions. If the temperature is held constant, the voltage is stable over time [Fig. 2(j)]. We carried out voltage measurements across probes U7 and U8 by interchanging the polarities of the nanovoltmeter leads [Fig. 2(k)]. In both cases, there were positive peaks.

The unconventional mechanism of nonreciprocal transport observed in our experiments is characterized by voltage signals symmetric in magnetic field. We postulate that the breaking of inversion symmetry required for this phenomenon results from a finite electric polarization within the niobium films. At the microscopic level, this can be described by a dipole moment distribution $\mathbf{P_{el}}(\mathbf{r})$ within the conducting electronic system ($\mathbf{r}$ being the position coordinate). A nonzero value of the average polarization $\overline{\mathbf{P_{el}}}$ implies the occurrence of nonreciprocal transport, with a finite value of experimentally measured α. A theoretical model to qualitatively explain the origin of a finite $\overline{\mathbf{P_{el}}}$ will be discussed next.

Moro *et al.* [24] have studied the electric deflection of cold clusters of Nb atoms (size ranging from 2 to 150 atoms). The clusters developed unusually large electric dipole moments at low temperatures. Interestingly, the dipoles were nonclassical in nature [24,25] and reflected a spontaneous-symmetry-broken ferroelectric state. These results offer a starting point to build an understanding of electric polarization in our devices. Niobium films realized with evaporation [26] and sputtering [22] techniques are composed of nanoscale grains with a large distribution of particle size. Durkin *et al.* [26] determined that superconductivity develops from a mechanism of rare-region onset. Bose *et al.* [22] observed that superconductivity disappeared for films with an average particle size of 8 nm, consistent with the Anderson criterion. At low temperatures, insulating behavior might be expected in very small grains a few nanometres in size [27], as well as in intergrain boundaries. We hypothesize that these insulating parts of the niobium film host nonclassical electric dipole moments (denoted by $\boldsymbol{\mu}$) which are free to orient in arbitrary directions. We treat the phenomenon of electric dipoles in small grains to be unrelated to the physics of superconductivity in larger grains. The following Hamiltonian describes the mutual interaction of the dipole moments:

$$H = -J \sum_{i,j} \boldsymbol{\mu}_i.\boldsymbol{\mu}_j - \mathbf{E_{ext}}.\sum_{\mathbf{i}} \boldsymbol{\mu}_{\mathbf{i}}. \tag{1}$$

J is the interaction parameter and $\mathbf{E_{ext}}$ is an external electric field which couples to the dipoles. $\boldsymbol{\mu}_i$ is the dipole moment of the ith insulating grain and the first summation ($\sum_{i,j}$) runs over pairs of adjacent dipoles. We consider the case $J > 0$, signifying ferroelectric coupling. When $\mathbf{E_{ext}}$=0, energy is minimized for a spontaneous-symmetry-broken state with all dipoles aligned parallel, resulting in a macroscopic moment $\overline{\boldsymbol{\mu}} = \sum_i \boldsymbol{\mu}_i$. However, the direction of $\overline{\boldsymbol{\mu}}$ is arbitrary. A small $\mathbf{E_{ext}}$ introduces a preferred direction leading $\overline{\boldsymbol{\mu}}$ to align parallel to it due to the coupling term in Eq. (1). The finite ferroelectric moment $\overline{\boldsymbol{\mu}}$ originating from dipoles in insulating parts of the niobium film induces a polarization in the conducting electronic system (arising from larger and more metallic grains). The electric field due to $\overline{\boldsymbol{\mu}}$ should be screened within the system of metallic free electrons. However, the neighborhood of the superconducting transition presents a different case. Theoretical studies [28,29] have shown that the chemical potentials of superconducting and normal states are different, as a consequence of which there will be a transfer of charge from one electronic subsystem to another if they coexist. This allows a mechanism for dipole moments to appear at the physical boundary of two different electronic phases when the superconducting transition occurs, resulting in the distribution $\mathbf{P_{el}(r)}$. In the presence of a background electric field due to $\overline{\boldsymbol{\mu}}$, the distribution $\mathbf{P_{el}(r)}$ can have a nonzero macroscopic average $\overline{\mathbf{P_{el}}}$. This provides a possible explanation of nonreciprocal transport in our devices.

We will now try to understand the phenomenon that the spontaneous voltage (V_s) peaks often do not change sign upon interchanging the voltmeter input connectors. Voltmeters used in practice may apply small signals on the sample being measured. One such signal is the input bias current [30] which flows between its terminals. This effect is negligible under most practical circumstances. The nanovoltmeter bias current is typically 60 pA, producing a drop of 60 nV per kΩ of external resistance. There might also be stray voltages due to charges accumulated across the input impedance and thermoelectric potentials in the internal circuitry. We speculate that it is such small undetermined signals, corresponding to $\mathbf{E_{ext}}$ in Eq. (1), which cause the polarity (but not the magnitude) of the spontaneous dc voltage peak across the sample to develop in a specific orientation, in correlation with the polarity of connectors at the voltmeter input. To verify this understanding, the circuit outlined in Fig. 2(l) was implemented. The device (with resistance R_s) is connected in parallel with a resistance R_p. When $R_p \ll R_s$, it shorts a large part of the external signal, leading the device to experience a much reduced $\mathbf{E_{ext}}$. Figure 2(l) shows the results of voltage measurement for two different configurations of voltmeter leads with $R_p = 67\ \Omega$. We observe voltage peaks of reduced magnitude (<1 μV). This is expected because the power delivered is V_s^2/R_p, requiring that V_s must reduce considerably for a small R_p on energetic grounds. The lineshape is different from usual cases, presumably because R_p provides a low impedance path for charge flow between the extremities of the superconductor. This distorts the polarization distribution $\mathbf{P_{el}(r)}$ affecting the rectification properties. The most important observation here is that the polarity of the V_s signal reverses sign for the two orientations of voltmeter leads. This shows that the usually observed positive polarity of voltage peaks (when no R_p is present) is a consequence of small signals within the voltmeter, which are unavoidable in practical circumstances. The polarity of the V_s signal is extremely susceptible to small external electric fields for choosing a preferred direction. This sensitivity is indicative of a mechanism of spontaneous symmetry breaking, which was outlined in our theoretical model.

The microstate of the system, described by the configuration of dipole moments, possibly varies from one experimental run to another. This explains the fact that the shapes of the voltage peaks differ from one set of measurement to another [as in Figs. 2(k) and 2(h)]. The peaks always occur within the width of the superconducting transition as determined from resistance measurements, which is consistent with the discussed theoretical model, and no exception to this rule has been observed.

It is worthwhile to recount one previous report of the observation of spontaneous voltage peaks in a different superconducting system. In experiments aimed at measuring nonlocal voltages in amorphous NbGe, finite voltage peaks were seen [31] close to the critical temperature of the superconducting transition. This phenomenon lacked a clear explanation. The striking features were that the peaks appeared at zero magnetic field and persisted even without an applied current [32]. These results have a close resemblance to the data shown in Fig. 2(i) of this Letter. It is plausible that the voltage peaks observed previously in amorphous NbGe arose from a rectification effect similar to the one seen in our Nb devices.

In summary, we observed spontaneous voltage peaks at the superconducting transition of plain Nb channels resulting from rectification of environmental fluctuations. The peaks are symmetric in the magnetic field and also occur at the critical temperature without an applied field. These results highlight an unconventional mechanism of nonreciprocal transport, involving the spontaneous development of an electric polarization within the superconducting film which breaks inversion symmetry. We can arrive at a qualitative understanding of our observations based on a hypothesis that insulating parts of the niobium films (nanosized grains and intergrain boundaries) host ferroelectric dipole moments at low temperatures. This reveals a striking similarity with the phenomenon of ferroelectric dipoles [24,25] observed in free niobium clusters. Experimental [33–35] and theoretical [36–38] works have previously suggested that there are many interesting questions regarding the impact of electric fields on superconductors which are yet to be fully understood. Our experiments show that nonreciprocal transport measurements can reveal the existence of electric polarization concomitant with superconductivity and provide new directions for research on these questions.

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