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Sign-Reversing Hall Effect in Atomically Thin High-Temperature Bi_{2.1}Sr_{1.9}CaCu_{2.0}O_{8+δ} Superconductors
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Sign reversing Hall effect in atomically thin high temperature superconductors

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We developed novel techniques to fabricate atomically thin Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ van der Waals (vdW) heterostructures down to two unit cells while maintaining a transition temperature $T_c$ close to the bulk, and carry out magnetotransport measurements on these vdW devices. We find a double sign change of the Hall resistance $R_{xy}$ as in the bulk system, spanning both below and above $T_c$. Further, we observe a drastic enlargement of the region of sign reversal in the temperature-magnetic field phase diagram with decreasing thickness of the device. We obtain quantitative agreement between experimental $R_{xy}(T, B)$ and the predictions of the vortex dynamics-based description of Hall effect in HTS both above and below $T_c$.

Tunable van der Waals (vdW) structures based on atomically thin superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO) crystals enables exploring unconventional electronic properties of high temperature superconductors (HTS) [1]. One of the most insightful tools to study properties of electronic systems is the Hall effect. However, the behavior of Hall resistance in HTS, in particular its sign change, remains poorly understood. As temperature, $T$, decreases through the fluctuation region approaching the transition temperature $T_c$, the Hall resistance decreases and changes its sign relative to that of the normal state. Then $R_{xy}(T)$ reverses sign again before vanishing at low temperatures [2, 3].

A rich theoretical lore attributes the Hall anomalies to either vortex pinning [4], details of the vortex core electronic spectrum [5, 6], hydrodynamic effects [7], superconducting fluctuations [8–10], Berry phase [11], and charges in the vortex core [12]. However, neither the explanation nor the consensus of the Hall behavior in the entire temperature range was achieved. A comprehensive explanation of the Hall sign reversal appeared in [13], which completely took into account both topological and normal excitation scattering effects, and especially the fact that the density of normal excitations at the vortex core differs from that far from the vortex. The results of [13] established that the sign-reversed Hall effect occurs in the temperature range where contribution from the vortex motion dominates over the effects from normal excitations and is controlled by the excess charge at the vortex core and the magnitude of the parameter $Δτ/h$, where $Δ(T)$ is the superconducting gap and $τ$ is the scattering time of normal quasiparticles.

In this letter, we report fabrication of superconducting (SC) atomically thin BSCCO crystals with strongly enhanced fluctuation effects and their magnetotransport properties. We observe Hall sign reversal which smoothly spans the superconducting transition, and persists both deep into the superconducting state and 5K above $T_c$. We present quantitative description of the observed phase boundary separating the normal and sign-reversed Hall domains [13] in terms of vortex dynamics in the entire temperature interval both below and above $T_c$, revealing a deep connection between vortex-like excitations above $T_c$ [14, 15] and superconducting fluctuations.

We prepare our few unit-cell (UC) thick BSCCO by mechanically exfoliating optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ in argon filled glovebox. After conventional nano-fabrication

Figure 1. Van der Waals BSCCO device. a. Optical image of Hall bar device, showing BSCCO with contacts and hexagonal boron nitride (h-BN) cover, as drawn in the inset below. b. Cross-sectional view of a typical device in scanning TEM. Columns of atoms are visible as dark spots. Black arrows point to location of bismuth oxide layers (darkest spots), while gray arrows show their extrapolated positions. c. Resistivity as a function of temperature for vdW devices of different thickness.
steps, BSCCO typically becomes insulating [16] due to chemical degradation [50] and oxygen escape [18]. We have developed a high-resolution stencil mask technique (See SI), allowing us to fabricate samples entirely in an argon environment without exposure to heat or chemicals, and subsequently sealed with a top hexagonal boron nitride (h-BN) layer. Figure 1a and b shows our typical Hall bar and a cross-sectional scanning TEM image of our vdW heterostructure, where dark spots are individual columns of atoms. The darkest of these are bismuth (arrows). While the outermost layers of BSCCO became amorphous, inner layers are left pristine, and retain $T_c$ close to the bulk value. The amorphous outer layers are likely the result of water vapor traces leaking through the h-BN/SiO$_2$ interface, and constrains us to devices above 2 UC.

Figure 1c shows the resistivity $\rho$ as a function of temperature $T$ for BSCCO devices between 2 - 10 UC. We find that at a given temperature $T$, resistivity $\rho$ increases as the thickness of the sample $d$ decreases. We have normalized our resistance data with the atomic force microscopy (AFM) thickness, which is sensitive to the highly resistive amorphous surface layer. The $\rho(T)$ dependence is linear in the normal region, consistent with BSCCO near optimal doping [19] and exhibits a SC transition, at temperature slightly lower than the bulk one [20].

To describe the SC transition in $\rho(T)$ and determine the transition temperature $T_c$, we employ the framework of superconducting fluctuations (SF) [21–23], accounting for all fundamental SF contributions to conductivity: Aslamazov-Larkin, the SF change in the density of states (DOS) of normal excitations, and the dominant Maki-Thompson contribution [23, 24], using both $T_c$ and the pair-breaking parameter $\delta = h/16k_B T \tau_\phi$ as fitting parameters. The phase-breaking time is assumed to be $\tau_\phi \sim T^{-1}$ [25], see details in SI. For all samples, the extracted $T_c$ (given in SI) is very close to the temperature of the inflection point, i.e. the temperature where $dR/dT$ is maximal [24, 26], and lies at the foot of $\rho(T)$. As a consistency check, numerous comparative studies [27, 28] of bulk HTS demonstrated that $T_c$ extracted from magnetic susceptibility agrees with the $T_c$ from the inflection point.

Figure 2a presents the Hall data for a 2 UC device (solid lines), and, as usual, the odd component of $R_{xy}(B)$ is shown in order to eliminate effects from device geometric imperfections. In the normal state far above $T_c$ ($T \geq 100$ K), the Hall resistance $R_{xy}$ is linear in applied magnetic field $B$. Figure 2b shows the quantity $(e dR_{xy}/dB)^{-1}$ measured at 100 K, which scales linearly with $d$, implying an excellent oxygen dopant retention in each CuO$_2$ plane, despite the fact that mobile oxygen dopants [18] escape from our crystals over time. The 3 UC sample, the only device fabricated and cooled down in the same day, contains a higher carrier density, which agrees with the slightly increased $T_c$ (Fig. 1c).

The Hall mobility $\mu_H = R_{xy}/B\rho_{xx}$ is shown in Fig. 2c. Below 5 UC, $\mu_H$ decreases with $d$, due to the increasing ratio of highly resistive (yet non-insulating) surface layers compared to pristine interior layers (see Fig. 1b), both of which contribute to the Hall and resistivity measurements in parallel. All our samples exhibit the trend $\mu_H \sim T^{-1}$ for $T \gg T_c$, suggesting that the normal carrier momentum relaxation time is $\tau_p \sim T^{-1}$ regardless of $d$.

Approaching $T_c$, $R_{xy}(B)$ becomes nonlinear (Fig. 2a). The first sign reversal is observed about 5K above $T_c$, up to 95K for our most highly doped sample (Fig. 2a and SI). The dip in $R_{xy}(B)$ becomes increasingly pronounced as temperature decreases and the region of negative sign extends from zero field to $B = 4.7$ T at about $T = 75$ K. Upon further cooling, $R_{xy}(B)$ flattens again and the $B$-interval of the negative $R_{xy}$ shrinks, until completely vanishing at $T \approx 60$ K (see also section F in SI). Then $R_{xy}(B)$ remains positive at all fields, until it disappears into the noise at $T \approx 40$ K.

The temperature evolution of $R_{xy}(T)$ at fixed $B$ (Fig. 3a) highlights a double sign reversal temperature interval. Figure 3b summarizes regions of sign reversal for the samples with similar doping and different thickness $d$. The $R_{xy}(T, B) < 0$ domain grows with decreasing $d$, while extending across and above $T_c$ in all our samples.

The Hall sign reversal in high-$T_c$ is usually well pronounced in the mixed state below $T_c$ extracted from the SF measurements a. Hall resistance for a 2 UC sample. The curves are vertically shifted for clarity, the horizontal dashed lines mark $R_{xy} = 0$. Below 60K, the Hall effect has the same sign as in the normal state. Above 60K the sign reversal appears at magnetic fields $B < 5$ T. Dashed and dash-dot lines show fits to the data (solid lines) b. Inverse Hall resistance increases linearly with sample thickness in our devices, demonstrating good oxygen dopant retention down to 2 UCs. Data taken at 100K. c. Device mobility increases as samples become thicker, eventually saturating at 5 UC.

Figure 2. Hall effect measurements a. Hall resistance for a 2 UC sample. The curves are vertically shifted for clarity, the horizontal dashed lines mark $R_{xy} = 0$. Below 60K, the Hall effect has the same sign as in the normal state. Above 60K the sign reversal appears at magnetic fields $B < 5$ T. Dashed and dash-dot lines show fits to the data (solid lines) b. Inverse Hall resistance increases linearly with sample thickness in our devices, demonstrating good oxygen dopant retention down to 2 UCs. Data taken at 100K. c. Device mobility increases as samples become thicker, eventually saturating at 5 UC.
framework, the temperature where Cooper pair lifetime becomes infinite \cite{19, 29}. In conventional superconductors, Hall sign reversal usually occurs in the Gaussian fluctuations regime at \( T > T_c \) \cite{30, 31}. However, there are experiments hinting at Hall sign reversal occurring slightly above \( T_c \) in 100-400 nm thick cuprate films \cite{32, 33}. In our atomically thin BSCCO flakes, the Hall sign reversal region persists well above \( T_c \) (by 5K). Importantly, in our 3 UC device with the highest \( T_c \), sign reversal persists up to 4.1 T at the onset \( T_c \approx 90 K \) of our bulk crystal \cite{20}, and up to \( T_{HSE} \approx 95 K \) (See SI section C), i.e. a few Kelvins above the highest \( T_c \) for the bulk Bi-2212 family.

That Hall resistance \( R_{xy}(T) \) does not exhibit any drastic changes when crossing \( T_c \) (Fig. 3) suggests the possibility of a unique universal description of the Hall effect over the entire experimental range of temperatures and magnetic fields. Such a universal description is provided by the time-dependent Ginzburg-Landau (TDGL) equation \cite{3}. In the fluctuation regime at \( T \gg T_c \), where fluctuational order parameter is small, TDGL can be linearized. In this Gaussian approximation, the Hall resistance can be calculated with \cite{10} accounting for SF effects. At \( T < T_c \), the electromagnetic response of superconductors is governed by vortex dynamics. In this regime, the GL functional can be expressed in terms of collective variables representing topological vortex excitations. As observed in \cite{2}, it is the change from normal carrier- to the flux flow-dominated transport that causes the sign reversal in Hall resistance. Since the sign reversal is observed above \( T_c \), one expects that the expansion of the TDGL with respect to vortex topological excitations will provide an adequate description of the Hall effect at temperatures from \( T > T_c \) down to zero. This program was realized in \cite{13}, where the Hall conductivity was derived as:

\[
\sigma_{xy} = \frac{\Delta^2}{E_F} \cdot n_b \cdot \frac{\epsilon_c}{B} ([\pi\Delta/(\hbar\tau)]^2 - \sin(\delta n)) + \sigma_{xy}^n(1 - g). \tag{1}
\]

Here \( n_0 \) and \( n_\infty \) are the normal carrier density inside and outside the vortex core respectively, and \( \delta n = n_0 - n_\infty \) is the excess charge inside the vortex; \( \tau \) is the relaxation time of the normal carrier in the vortex core; and parameter \( g \) expresses the SC fraction of the carriers. The second term in the rhs of Eq. (1) ensures a smooth transition to Hall conductivity dominated by normal carriers. We consider a two-fluid model of a \( d \)-wave symmetry superconductor \cite{34} so that \( g(T) = 1 - (T/T_c)^2 \). Where the value of \( T_c \) was previously determined from the analysis of \( R_{xy}(B, T) \) with SF description.

This result makes apparent that the physical origin of the Hall effect sign change is the excess charge \( \delta n \) of the vortex core, which is of order \( n_0(\Delta/E_F)^2 \) \cite{13, 32}. The sign of the vortex contribution is controlled by the relation between \( \sin(\delta n) \) and \( \pi \Delta \). In the regime \( T < T_c \), this empirically fixes \( \sin(\delta n) = 1 \). Then, the first term in Eq. (1), the vortex core contribution \( \sigma_{xy}^v \), can be negative as \( \Delta(T) < \hbar/\tau \). Furthermore, we note that \( \sigma_{xy} \sim B^{-1} \) while \( \sigma_{xy}^n \sim B \). Therefore, the total Hall sign reversal is expected at low magnetic fields, where negative vortex contribution \( \sigma_{xy}^v \) dominates the positive normal carrier contribution \( \sigma_{xy}^n \).

Using Eq. (1), we describe the phase boundary of the Hall sign reversed region in Fig. 3(b) for all the samples under study. The sign reversal locus, \( R_{xy}(T, B) = 0 \), follows from Eq. (1) and is defined by the relation:

\[
B^2 = \left( \frac{\Delta}{E_F} \right)^2 \frac{n_0 c \left[ (\Delta(T)/\hbar\tau)^2 - 1 \right]}{S_{xy}^n} \cdot \frac{\epsilon_c}{B} \cdot \frac{1 - g}{1 - g}. \tag{2}
\]

Where we estimate the normal contribution \( \sigma_{xy}^n \) using the empirical observation \( \sigma_{xy} = S_{xy}^n(T) \cdot B \) in the normal state far enough from \( T_c \), where \( S_{xy}^n(T) \propto T^{-2} \) (see Fig. 4 in SI), we extrapolate this dependence to low temperatures. Then, we fit

\[\text{Figure 3. The double sign change. a. Temperature dependencies } R_{xy}(T) \text{ at fixed magnetic fields for the 2UC device. Fits above (dash-dot) and below (dashed lines) } T_c \text{ are superimposed on experimental data (symbols). Inset: Superconducting gap extracted from fits for all samples using Eq. (1). } T_c \text{ is the temperature extracted from analysis of } R_{xy}(T) \text{ in the framework of superconducting fluctuations (SF) } b. \]

\[\text{The Hall sign reversal phase diagram. Shading shows Hall resistance } R_{xy}(B, T) \text{ for a 2UC device with } T_c = 81.5 K. \text{ Blue region shows the area of negative Hall resistance. Symbols show the locus } R_{xy} = 0 \text{ for different thicknesses, and the lines are generated from fits to } R_{xy} = 0 \text{ using Eq. (2) [13] (solid) and using Eq. (3) (dash). As thickness decreases, the Hall sign reversed region becomes larger.}\]
our data shown in Fig. 3(b) with Eq. (2), using as fitting parameters \( \tau \) and \( n_0/E_F^2 \) (numerical values of all parameters are given in Table I in SI). We obtain the relaxation rate of the normal carriers in the vortex core \( \tau \approx 0.08 \) ps. This agrees with the quasiparticle lifetime estimated from the scanning tunneling spectroscopy of the vortex cores in BSCCO [35] observing normal quasiparticle excitations at \( E \approx 7 \) meV, giving the crude estimate \( \tau \approx h/E \approx 0.1 \) ps. The value \( n_0/E_F^2 \approx \left(1 - 2\right) \cdot 10^{21} \text{cm}^{-3}\text{eV}^{-2} \) is in satisfactory agreement with the widely accepted value \( n_0 \approx 10^{21} \text{cm}^{-3} \) in cuprates [36] and with the fact that \( E_F \) of cuprates is often an order of magnitude larger than the superconducting gap \( \Delta(0) \) [37] which is \( \Delta(0) \approx 0.02 \) eV in our case. For the temperature dependence \( \Delta(T) \), we take the temperature dependence of the \( d \)-wave gap (with \( \Delta(0)/k_BT_{HSR} = 2.15 \)) [38] where \( T_{HSR} \) is the upper temperature of the onset of the Hall sign reversal (see Table in SI). The \( d \)-wave description of \( \Delta(T) \) is also supported by STM measurements on BiO terraces in BSCCO [39], although tunnel spectra of exposed CuO terraces suggests a nodeless SC gap [39, 40]. Temperature dependencies of superconducting gap \( \Delta(T)/T_c \) vs. \( T/T_c \) are shown in inset of Fig. 3a for all samples. Note that \( T_{HSR} \) determined from our fits appeared to be higher than \( T_c \), implying nonzero \( \Delta(T_c) \), which is in agreement with experimental observations in tunneling [41] and in angle-resolved photoemission spectroscopy (ARPES) [42].

Equation (2) for the dome-shaped sign reversal phase boundary correctly describes the sign reversal enhancement as samples become thinner (Fig. 3). As the mobility \( \mu_H \) decreases with thickness (Fig. 2c), \( \sigma_{xy}^H \) is suppressed in turn. Since \( \mu_H \) is in the denominator in Eq. (2), the decrease of \( \mu_H \) leads to enhancement of dome size. In other words, the contribution from topological excitation has more effect on the conductivity \( \sigma_{xy} \) when the normal component \( \sigma_{xy}^H \) decreases (see Eq. 1).

The curve \( R_{xy}(B, T) = 0 \) defined by Eq. (2) demonstrates an excellent agreement with the experimental data shown in Fig. 3b both for \( T < T_c \) and for \( T > T_c \). Using the same fitting parameters we compare the whole \( R_{xy} \) evolution with the vortex expansion of the TDGL. Figure 2a and 3a show the fits of \( R_{xy} \) at fixed \( T \) and \( B \) respectively in dashed lines, calculated according to Eq. (1) using \( \rho_{xy}^H = \sigma_{xy}^H \cdot \rho_{xx}^H \). The vortex dynamics description agrees well with the experiment in a wide region in temperature \( T < T_c \) and magnetic field. For \( T > T_c \) the agreement is still fair, however, we observe some deviation of theoretical curve from experimental \( R_{xy} \) (see curve at 80 K in Fig. 2a)), the deviation growing with increasing temperature [43].

To cross-check the applicability of the vortex-based description of \( R_{xy}(B) \) and \( R_{xy}(T) \) at \( T > T_c \), we employ the superconducting fluctuation expansion of TDGL, using the smallness of the order parameter in the fluctuation regime. Qualitatively, SF are Cooper pairs with a finite lifetime, arising above \( T_c \). Under applied magnetic field, these pairs rotate around their center of mass and can be viewed as elemental current loops. The external current exerts Magnus force moving these loops along the circular paths. This gives rise to Hall voltage opposite to that from the normal carriers. The SF contribution to Hall conductivity manifests as a negative correction \( \delta \sigma_{xy} \) to the positive normal component \( \sigma_{xy}^H \) [10, 21]:

\[
\delta \sigma_{xy} = \sigma_{xy}^H + \delta \sigma_{xy}. 
\]

Expression for \( \delta \sigma_{xy} \) in the Gaussian approximation [10] is:

\[
\delta \sigma_{xy} = \frac{2e^2 k_B T}{\hbar d} \xi f(D, B, T) \tag{3}
\]

where \( D \) is the normal carrier diffusion coefficient evaluated as \( D \approx \frac{1}{2} \mu_H E_F \) (see SI section E); \( f \) is a dimensionless function (see SI for explicit form); \( \xi \) is a parameter accounting for particle-hole asymmetry in the time-dependent Ginzburg-Landau equation. The parameter \( \xi \) is expressed as the change of \( T_c \) with respect to the chemical potential \( \mu \): \( \xi = -\frac{1}{2} \partial \ln T_c / \partial \mu \approx 1/(\gamma E_F) \) [10, 21, 44]. Here \( \gamma \) is the dimensionless coupling constant parameterizing the attractive electron-electron interaction that induces superconductivity. As temperature decreases, the SF contribution \( \delta \sigma_{xy} \) increases, leading to the sign change of \( \sigma_{xy} \) as soon as \( \sigma_{xy} \) starts to dominate [30, 31, 45]. The Hall resistance \( R_{xy}(B) \) and \( R_{xy}(T) \) at \( T > T_c \) is nicely described by the SF description of Eq. (3) (dash-dotted line in Fig. 2a and 3a), where the values of fitting parameter \( \gamma E_F \) (see SI) correspond to \( \gamma < 1 \) (the weak coupling limit) and \( E_F \) previously evaluated from fits of \( R_{xy}(B, T) = 0 \) with Eq. (2). The phase boundary for \( T > T_c \) is also accurately captured by the SF description in Eq. (3) (Fig. 3b, dashed line). Remarkably for \( T > T_c \), the phase boundary \( \sigma_{xy}(B, T) = 0 \) agrees with both vortex and SF TDGL asymptotes. The agreement between the values of \( E_F \) and fits of the phase boundary provides a crosscheck ensuring that vortex description of Eq. (2) works fairly well at \( T > T_c \). Thus our findings support the idea that vortex-like excitations survive above \( T_c \) [46] in full concert with Nernst effect observations [14, 15]. Our results apply to any bulk HTS with layered structure. Also, since disorder enters through the scattering time, our conclusions remain valid for disordered low-\( T_c \) films, see, for example, [47, 48].

In conclusion, we developed van der Waals assembly techniques specialized to the cuprates. We fabricated few-unit-cell \( \text{Bi}_2\text{Sr}_1\text{Y}_0\text{Cu}_2\text{O}_8 \) crystals, where an appreciable enhancement of the Hall sign reversal with the system’s thinning was observed. We demonstrated that the Hall resistance sign reversal occurs both below and above \( T_c \) and is well described in terms of vortex dynamics across the entire temperature interval. In the fluctuation region above \( T_c \), the sign reversal is equally well described by superconducting fluctuations formalism which cross checks our results and connects vortex-like excitations above \( T_c \) and superconducting fluctuations.

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