Discovery of a Cooper-pair density wave state in a transition-metal dichalcogenide

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Pair density wave (PDW) states are defined by a spatially modulating superconductor order parameter. To search for such states in transition-metal dichalcogenides (TMDs), we used high-speed atomic-resolution scanned Josephson-tunneling microscopy. We detected a PDW state whose electron-pair density and energy gap modulate spatially at the wave vectors of the preexisting charge density wave (CDW) state. The PDW couples linearly to both the s-wave superconductor and the CDW and exhibits commensurate domains with discommensuration phase slits at the boundaries, conforming those of the lattice-locked commensurate CDW. Nevertheless, we found a global \(\delta\phi \approx \pm 2\pi/3\) phase difference between the PDW and CDW states, possibly owing to the Cooper-pair wave function orbital content. Our findings presage pervasive PDW physics in the many other TMDs that sustain both CDW and superconducting states.

This state also breaks gauge symmetry, and its mean-field order parameter is \(\langle C_x^+ C_x^- + q_x \rangle\). Sophisticated atomic-scale visualization of TMD states by using single-electron tunneling (13–16) has revealed CDW quantum phase transitions (13), a CDW Bragg glass (14), interfacial band alignment (15), and strain control of the CDW state (16). But to detect and image a PDW state in TMDs remained an experimental challenge.

Experimentally, the total electron-pair density \(\rho_{pdw}(r)\) might be visualized by measuring Josephson critical-current \(I_{J}(r)\) to a superconducting tunneling spectroscopy (STM) tip (17) because \(\rho_{pdw}(r) \approx I_{J}(r)R_{pdw}^{(2)}(r)\), where \(R_{pdw}\) is the normal-state junction resistance (18, 19). But this has proven impractical because the thermal fluctuation energy \(k_B T\) typically exceeds the Josephson energy \(E_J = \Phi_0 I_{J}/2\pi\), where

\[
I_{J} = \frac{\pi \Delta(T)}{2 e R_{N}} \tanh \left[ \frac{\Delta(T)}{2 k_B T} \right]
\]

\(k_B\) Boltzmann constant; \(T\) temperature; 2e electron-pair charge; and \(\Phi_0\) magnetic flux quantum). Instead, when \(E_J < k_B T\), the tip-sample Josephson junction exhibits a phase-diffusive (20–22) steady state at voltage \(V\) and electron-pair current

\[
I_{CP}(V) = \frac{1}{2} \frac{2 e Z V}{V^2 + V_0^2}
\]

Here, \(V_0 = 2 e k_B T/\hbar\), where \(Z\) is the high-frequency impedance in series with the voltage source and \(\hbar\) is Planck’s constant divided by 2\(\pi\).

\[
dI_{CP}/dV = g(V) = \frac{1}{2} \frac{2 e Z (V_0^2 - V^2)}{(V_0^2 + V^2)^2}
\]

This yields \(g(0) \approx I_{J}^2\) (fig. S1) [(23), section 1]. Thus, spatially resolved measurements of \(g(0, r)\) can provide a practical means (24–28) to image \(I_{J}(r)\), so that the electron-pair density can then be visualized as \(\rho_{pdw}(r) = g(r, 0)R_{pdw}^{(2)}(r)\) \(\propto \rho_{pdw}(r)\) [(23), section 1].

We studied bulk crystals of 2H-NbSe2, a quasi–two-dimensional TMD with a robust CDW state (29). It has a hexagonal layered structure with Se-Se separation \(d\) and a Fermi surface with pockets surrounding the \(\Gamma\) and \(K\) points (fig. S2). The CDW phase transition at \(T_{c} \approx 33.5\) K generates crystal and charge density modulations at three in-plane wave vectors \(\mathbf{Q}_n^c = \{(1, 0); (1/2, \sqrt{3}/2); (-1/2, \sqrt{3}/2)\} 2\pi/3d_0\) \(d_0 = \sqrt{3}d/2\) is the unit cell dimension), and the s-wave superconductivity (SSC) transition at \(T_{c} \approx 7.2\) K completely gaps the Fermi surface. We used atomic-resolution superconducting scanning tips made of Nb (17) with a standard tip-energy gap \(\Delta_{tip} = 0.9\) meV (fig. S3).

A typical topographic image \(T(r, V)\) of the Se-termination layer of NbSe2, when using such tips is shown in Fig. 1A, with the CDW modulations appearing as 3\(d_0\) periodicity amplifications [Fig. 1A, inset, \(T(Q, V)\)] (13, 14). A typical differential tunneling conductance spectrum \(dI/dV\) \(|g(V)|\) is shown in Fig. 1B. To simultaneously visualize the CDW, SSC, and any putative PDW states, a dynamic range exceeding \(10^8\) is required in the tip-sample voltage, spanning the CDW range from above \(50\) mV (fig. 1B), to the SSC energy gap range \(1\) mV (Fig. 1C), to the Josephson pair-current range approaching \(10\) \(\mu\)V (Fig. 1, D and E). Visualizing the quasiparticle densities \(N_{pdw}(r)\) of both CDW and SSC uses single-electron tunneling at energies indicated with the red and green arrows in Fig. 1, B and C, respectively. Visualizing electron-pair density \(N_{pdw}(r)\) of the condensate uses the phase-diffusive Josephson tunneling current \(I_{CP}(V)\) or \(g(0)\), indicated with the blue arrows in Fig. 1, D and E.

At \(T = 290\) mK, we first image \(N_{pdw}(r) = g(r, -20\) mV) at \(V = -20\) mV, where CDW intensity is strong (13), with the results shown in Fig. 2A. Next, we imaged the normal-state resistance (fig. S4) of the tip-sample Josephson junction \(R_{N}(r) = I_{J}^2(r, -45\) mV) (Fig. 2B). Third, we studied the electron-pair current by measuring \(g(r, 0)\) (Eq. 6) (Fig. 2C). All four independent images \(T(r, V)\), \(N_{pdw}(r)\), \(R_{N}(r)\), and \(g(r, 0)\) are registered to each other with precision of \(\delta V = \delta y \leq 15\) pm (fig. S5) [(23), section 2]. This constitutes a typical data set for visualizing the crystal, CDW, SSC, and PDW states simultaneously; its acquisition required developing high-speed scanned Josephson-tunneling microscopy (SJTM) imaging protocols (fig. S6) [(23), section 3]. Eventually, to visualize the electron-pair density, we used the data in Fig. 2, B and C to derive \(N_{pdw}(r) = g(r, 0)R_{pdw}^{(2)}(r)\) (Fig. 2D). Here, we see electron-pair density modulations at three in-plane wave vectors \(\mathbf{Q}_n^c = \{(1, 0); (1/2, \sqrt{3}/2); (-1/2, \sqrt{3}/2)\} 2\pi/3d_0\).

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In a PDW state, the energy gap $\Delta(r)$ should also modulate at $Q_F$ (Eq. 3). We define the total gap $|\Delta(r)| = |\Delta_F(r) + \Delta|$ to be half the energy separation between two coherence

Fig. 1. Simultaneous single-electron and electron-pair tunneling spectroscopy.

(A) Topographic image $T(r)$ of Se-termination surface of NbSe$_2$ measured at $T = 290$ mK. (Inset) The Fourier transform $T(q)$ with Bragg peaks $Q_B = \{(1,0); (1/2,\sqrt{3}/2); (-1/2,\sqrt{3}/2)\}2\pi/a_0$ indicated with gray circles and the CDW peaks $Q_C = \{(1,0); (1/2,\sqrt{3}/2); (-1/2,\sqrt{3}/2)\}2\pi/3a_0$ indicated with black circles. (B) Typical differential tunnel conductance spectrum $g(V) = dI/dV(V)$ from a Nb scan-tip to NbSe$_2$ surface at $T = 290$ mK. The range of energies at which CDW modulations are intense in $g(V)$ is indicated approximately with red arrows.

(C) Energy range in (B) is zoomed to show typical $g(V)$ characteristic owing to the combination of the superconducting energy gaps $\Delta_T$ of the Nb tip and $\Delta$ of the NbSe$_2$. The range of energies at which superconducting coherence peaks are intense in $g(V)$ is indicated with green arrows.

(D) Measured electron-pair tunnel current $I_{CP} (V)$ in the phase-diffusive Josephson effect energy range $|E| \lesssim 100$ meV, with the range of energies at which electron-pair current is maximum $\langle I_{m} \rangle$ indicated with blue arrows.

(E) Energy in (C) is zoomed to show phase-diffusive Josephson effect energy range, and the measured $g(V)$ whose $g(0) \propto I_J^2$ from Eq. 6 is indicated with a blue arrow.
peaks minus $|\Delta_{\text{F}}|$. Our measured $|\Delta_{\text{F}}(\mathbf{r})|$ then exhibits modulations at three wave vectors $\mathbf{Q}_{c}^{i} = (1, 0); (1/2, \sqrt{3}/2); (-1/2, \sqrt{3}/2)2\pi/3a_0$ (fig. S7) [(23), section 4]. This confirms independently, by use of single-electron tunneling, the existence of a PDW state in NbSe$_2$. Its gap modulation amplitude $|\Delta_{\text{F}}| < 0.01|\Delta_{\text{C}}|$ [(23), section 4]. A plot of the measured Fourier amplitudes of simultaneous $N_{\text{C}}(\mathbf{q})$ and $N_{\text{CP}}(\mathbf{q})$ in the directions of $\mathbf{Q}_{c}^{i} = \mathbf{Q}_{c}^{i}$ is shown in Fig. 3A. The key maxima occur near $|\mathbf{q}| = 2\pi/3a_0$, establishing quantitatively that $|\mathbf{Q}_{c}^{i}| = |\mathbf{Q}_{c}^{i}| \pm 1\%$. But, although imaged in precisely the same field of view (FOV), the charge density modulations (Fig. 2E) and electron-pair density modulations (Fig. 2F) appear distinctly different, with normalized cross correlation coefficient $\eta = 0.4$.

Possible microscopic mechanisms for a PDW state include Zeeman splitting (30, 31) of a Fermi surface (not relevant here) and strongly correlated electron-electron interactions generating intertwined CDW and PDW states (32, 33). But whatever the microscopic PDW mechanism for NbSe$_2$, Ginzburg-Landau (GL) theory allows a general analysis of interactions between SSC and CDW states. Consider a diabatic GL free-energy density

$$F = F_{\text{SSC}} + F_{\text{CDW}} + F_{\text{PDW}} + \lambda_{S}\lambda_{C}\lambda_{D} (\text{c.c.})$$

(7)

Here, $F_{\text{SSC}}$, $F_{\text{CDW}}$, and $F_{\text{PDW}}$ are the free energy densities of a SSC state (Eq. 2), a CDW state (Eq. 1), and a PDW state (Eq. 3), respectively. The term $\lambda_{S}\lambda_{C}\lambda_{D}$ represents lowest-order coupling of the SSC and CDW states with a PDW and induces $A_{\text{PDW}}(\mathbf{r})$ at wave vectors $\mathbf{Q}_{c}^{i} = \mathbf{Q}_{c}^{i}$ owing to interactions of $\rho_{\text{PDW}}^{i}(\mathbf{r})$ and $\Delta_{\text{F}}$. But the relative spatial arrangements of $\rho_{\text{PDW}}^{i}(\mathbf{r})$ and $\Delta_{\text{F}}$ are ambiguous because if $\rho_{\text{PDW}}^{i}(\mathbf{r}) \propto \Delta_{\text{F}}^{i}(\mathbf{r})$, the charge density and electron-pair density modulations of the CDW and PDW for all three wave vectors $\mathbf{Q}_{c}^{i} = \mathbf{Q}_{c}^{i}$ (fig. S10). Shown in Fig. 4A is simultaneously measured $A_{\text{PDW}}^{i}(\mathbf{r})$ from Fig. 2A, and shown in Fig. 4B is the simultaneously measured $A_{\text{PDW}}^{i}(\mathbf{r})$ from Fig. 2D. Both show nanoscale variations in the magnitude of their order parameters that are spatially alike, which is consistent with Eq. 7. Shown in Fig. 4, C and D, are the $\Phi_{\text{PDW}}^{i}(\mathbf{r})$ and $\Phi_{\text{PDW}}^{i}(\mathbf{r}) - 2\pi/3$ simultaneously obtained with $\Phi_{\text{PDW}}^{i}(\mathbf{r})$ and $\Phi_{\text{PDW}}^{i}(\mathbf{r})$ in the same FOV as Fig. 1A with pixel size ~30 pm at $T = 290$ mK. (Inset) $N_{\text{CP}}(\mathbf{q})$, with CDW peaks indicated with red circles. (B) Simultaneously measured $R_{o}(\mathbf{r}) = f^{-1}(\mathbf{r}) - 4.5$ mV as in (A). The purpose of this measurement is to establish the normal-state tip-sample junction resistance. (B) Simultaneously measured $g(r, 0) = I_{\text{PDW}}(r)$ as in (A). (C) Pure CDW charge density modulations $N_{\text{C}}(\mathbf{r})$ from (D). These are visualized at wave vectors $\mathbf{Q}_{c}^{i} = \mathbf{Q}_{c}^{i}$. (D) Measured electron-pair density $N_{\text{CP}}(\mathbf{r}) = \rho_{\text{PDW}}^{i}(\mathbf{r})$ from (B) and (C). (Inset) $N_{\text{SSC}}(\mathbf{q})$, with CDW peaks indicated with blue circles. $N_{\text{C}}(\mathbf{r})$ are indicated with blue circles. (E) Pure CDW charge density modulations $N_{\text{C}}(\mathbf{r})$ from (D). These are visualized at wave vectors $\mathbf{Q}_{c}^{i} = \mathbf{Q}_{c}^{i}$.
Similarly the azimuthally averaged RMS amplitude of all three PDW modulations measured amplitudes of charge density modulations at $Q_i$ (red), centered on the vortex core symmetry point, and similarly the azimuthally averaged RMS amplitude of all three PDW modulations $A^\text{RMS}(r)$. From Fig. 4, C and D, and in Fig. 4F, we show a combined histogram of all $|\delta \Phi^i(r)|$ ($i = 1, 2, 3$). Hence, the relative spatial phase of the PDW and CDW states is globally $|\delta \Phi| = \pm 2\pi/3$. Experimentally measured $N^1_r(r)$ and $N^2_r(r)$ are shown in Fig. 4G, merging with simultaneously measured topography $T(r)$ from the same FOV (Fig. 2, E and F, yellow boxes), revealing that an $a_0$ displacement between $N^1_r(r)$ and $N^2_r(r)$ generates this universal $\pm 2\pi/3$ phase shift.

So, what generates and controls this complex new PDW state at atomic scale? First, Bloch-state modulations at crystal-lattice periodicity will lead inevitably to lattice-periodic modulations of $N^1_r(r)$, $N^2_r(r)$, and $\Delta(r)$ ([25], section 7). However, at a more sophisticated and specific level, a multiband plus anisotropic energy-gap theory of NbSe$_2$ has been developed to describe superconductive electronic structure modulations at the atomic scale ([36]). Beyond this, lattice strain is important in CDW physics of TMD materials ([13, 16]). Lattice-locked $3 \times 3$ commensurate CDW domains occur in NbSe$_2$, separated by discommensurations at which the CDW phase jumps by $\delta \Phi = \pm 2\pi/3$ ([28]). We detected these $\delta \Phi = \pm 2\pi/3$ discommensurations, for example, in $\Phi^1_r(r)$ (Fig. 4C and fig. S11) and found $\delta \Phi = \pm 2\pi/3$ phase slips for the PDW state at virtually identical locations, along its domain boundaries in Fig. 4D. This might be expected if the PDW is induced by the CDW coupling to the superconductivity because the PDW domains would replicate those of the preexisting CDW. Moreover, the interstate phase-difference $|\delta \Phi| = |\Phi^1_r(r) - \Phi^2_r(r)| = \pm 2\pi/3$ occurs universally (Fig. 4, C and D), not just at the commensurate domain boundaries. Hence, the simplest overall explanation is that the global phase shift $|\delta \Phi|$ does not originate from an independent lattice-lock-in of the PDW ([22], section 8).

As to atomic-scale interactions between the CDW and the SSC states, one must consider Cooper pairing in the presence of the CDW periodic potential $V(r)$. Solving the linearized superconducting gap equation does generate a nonzero $\Delta(r)$ with $Q_C = Q_{\text{CC}}$ (37). More intuitively, electron pairing occurs not only at momenta $(k, -k)$ but also $(k + G, -k)$ and $(k, -k + G)$, where $G$ is a reciprocal-lattice vector of the CDW state: $G = mQ_C; m = 0, \pm 1, \pm 2, \ldots$ (fig. S12). The consequent electron-pair density at lowest order in $G$ ([22], section 9) is

$$\rho_P(r) = \cos \left( Q_C \cdot r + \phi^Q_C + \delta \Phi \right)$$

Thus, the electron-pair density modulates spatially at the wave vectors $\pm Q_C$ owing to the finite center-of-mass electron-pair momentum ($\pm Q_C$) imposed by the CDW. Moreover, this same approach shows that a phase difference $|\delta \Phi| = |\Phi^1_r - \Phi^2_r|$ is determined by the wave vector $k$ of the electron-pair wave function ([22], section 9). Last, at the single-atom scale, we found that impurity atoms leave the PDW state virtually unperturbed.
(fig. S13), implying that Anderson’s theorem also pertains to an s-wave PDW.

The techniques and observations reported here herald abundant and exciting PDW physics in the many TMDs that, like NbSe₂, sustain both CDW and superconducting states.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Supplementary Text
Figs. S1 to S16
References (39–55)
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Imaging an exotic state
Among the most intriguing of the many phases of cuprate superconductors is the so-called pair density wave (PDW) state. PDW is characterized by a spatially modulated density of Cooper pairs and can be detected with a scanning tunneling microscope equipped with a superconducting tip. Liu et al. used Josephson tunneling microscopy, modified for the task, to detect PDW in niobium diselenide, a superconductor with a layered hexagonal structure. The PDW state is expected to appear in other transition metal dichalcogenides as well.

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