Long-Range Ordered Amorphous Atomic Chains as Building Blocks of a Superconducting Quasi-One-Dimensional Crystal

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Crystalline and amorphous structures are two of the most common solid-state phases. Crystals having orientational and periodic translation symmetries are usually both short-range and long-range ordered, while amorphous materials have no long-range order. Short-range ordered but long-range disordered materials are generally categorized into amorphous phases. In contrast to the extensively studied crystalline and amorphous phases, the combination of short-range disordered and long-range ordered structures at the atomic level is extremely rare and so far has only been reported for solvated fullerenes under compression.[1, 2] Here, we report on our creation and investigation of a superconducting quasi-one-dimensional (quasi-1D) material with long-range ordered amorphous building blocks. Using a diamond anvil cell, we compressed monocrytalline (TaSe$_4$)$_2$I and created a system where the TaSe$_4$ atomic chains are in amorphous state without breaking the orientational and periodic translation symmetries of the chain lattice. Strikingly, along with the amorphization of the atomic chains, the insulating (TaSe$_4$)$_2$I becomes a superconductor. Our data provide critical insight into a new phase of solid-state materials. Our findings demonstrate a first ever case where superconductivity is hosted by a lattice with periodic but amorphous constituent atomic chains.
The linear chain compound (TaSe$_4$)$_2$I has drawn considerable attention due to its intriguing electronic properties correlated to the quasi-1D structure. TaSe$_4$ chains, parallelly aligned in the c-axis and separated by strands of iodine atoms, serve as the building blocks of this paradigmatic quasi-1D material (Figure 1a). Under ambient conditions, (TaSe$_4$)$_2$I has a body-centered tetragonal unit cell (space group I422, No. 97), containing two adjacent chains with four TaSe$_4$ units in each chain and four halogen I atoms. Theoretical calculations revealed that the electronic properties of (TaSe$_4$)$_2$I are mainly determined by the interaction between the Ta atoms along the chain direction (c-axis). In the case of an overlap between the Ta 5$dz^2$ orbitals, the linear chain compound has a pancakes-like Fermi surface perpendicular to the chain direction, resulting in an extreme anisotropy in its electronic properties.

Furthermore, (TaSe$_4$)$_2$I has also been proven to be an ideal host of quasi-1D charge density waves (CDW). Due to the instability of the atomic lattice along the c-axis, the TaSe$_4$ chains demonstrate periodic modulations of the electron density, giving rise to various CDW-correlated phenomena in the electrical transport, magnetic and optical properties of (TaSe$_4$)$_2$I. For example, around the CDW transition temperature $T_p$ ca. 260 K, a kink was observed in both its electrical resistivity and magnetic susceptibility. Very recently, an exotic axionic CDW state has also been reported for this material. Due to the formation of fluctuating CDW, (TaSe$_4$)$_2$I even showed a steep decrease in the optical absorption at room temperature. These experimental results testified the strong intrachain confinement of electrons and thus the quasi-1D nature of (TaSe$_4$)$_2$I.

In this research, we use monocrystalline (TaSe$_4$)$_2$I as the starting material for the realization of a new quasi-1D phase with advanced electronic properties. By applying high pressures to
monocrystalline (TaSe$_4$)$_2$I using diamond anvil cells (see Experimental Section), for the first time, we systematically investigated the pressure-induced evolution of the structural and electronic properties of (TaSe$_4$)$_2$I through a combination of synchrotron X-ray diffraction (XRD), Raman scattering, electrical transport, and magnetic susceptibility measurements. When increasing the applied pressure up to ca. 20 GPa, we realized the amorphization of the constituent atomic chains of (TaSe$_4$)$_2$I without breaking the long-range order of the chain lattice. The as-prepared material with a combination of short-range disorder and long-range order demonstrates a new solid-state phase other than conventional crystalline or amorphous structures. Furthermore, upon the amorphization of the atomic chains, superconductivity emerged in our newly created system. This counterintuitive phenomenon brings attention to the Cooper pairing in quasi-1D materials disordered at the atomic level.

We investigated the pressure-induced evolution of the structure of (TaSe$_4$)$_2$I using XRD with a wavelength of $\lambda = 0.4133$ Å. Figure 1b shows the XRD spectra measured under applied pressures up to 36.3 GPa at room temperature. At 0.5 GPa, all the XRD peaks are well indexed by the space group $I422$ (SG No. 97), indicating the same (TaSe$_4$)$_2$I structure as that under ambient pressure (see Figure S1 for the fitting profile, Supporting Information).\cite{8, 16} Further increase of the applied pressure up to 17.9 GPa gives rise to the shift of the Bragg peaks to larger angles, due to the lattice shrinkage, as shown in the pressure dependences of the lattice parameters, $a$ and $c$, in Figure 1c.

Above 21.6 GPa, apart from the formation of a broad diffusive peak at ca. 9.8 degrees, the Bragg peaks other than (110), (200) and (220) all disappear from the XRD spectra (Figure 1b). These phenomena indicate that the applied high pressures introduced amorphous phases into the material.\cite{1, 2} Taking into account the facts that the sharp profile of the (110) peak is preserved...
throughout the structural evolution, and the TaSe$_4$ chains are the main blocks defining the (110) plane, we note that the amorphization took place only in the atomic chains without breaking the long-range periodic translation symmetry of the chain lattice. Accordingly, the monocristalline (TaSe$_4$)$_2$I was transformed into a short-range disordered but long-range ordered phase under high pressures, i.e., combination of amorphous and crystalline structures. The amorphization of the constituent atomic chains is irreversible upon decompression.

Figure 1d shows the pressure dependences of the distance between the adjacent TaSe$_4$ chains, $d_{\text{inter}}=a/\sqrt{2}$, and the diameter of the TaSe$_4$ chains, $d_{\text{intra}}$, extracted from the fitting of the XRD data (see Experimental Section). In contrast to the continuous decrease of $d_{\text{inter}}$, $d_{\text{intra}}$ is rather inert to the applied pressure below ca. 8 GPa. Correspondingly, as shown in the pressure dependence of $d_{\text{inter}}/d_{\text{intra}}$ (Figure 1e), the quasi-1D nature of the system was first diminished and then restored above 8 GPa.

To gain insight into the amorphization of the atomic chains, we performed Raman scattering measurements under different pressures to investigate the local lattice symmetry. Figure 2a shows the Raman spectra measured in a configuration by aligning the polarization direction of the incident light, $E_i$, parallel to the c-axis (see Experimental Section). The Raman-active modes observed at 1.2 GPa are in good agreement with the data of monocristalline (TaSe$_4$)$_2$I at ambient pressure (see Figure S2 and Table S1 for detailed analysis of the modes, Supporting Information). Consistent with our XRD data, the absence of Raman-active modes above ca. 20 GPa clearly indicates the occurrence of amorphization in the atomic chains.
The breaking of the local lattice symmetry is reflected in the pressure-induced evolution of the Raman-active modes, e.g., $A_{16}^6$ and $A_{17}^7$. Both $A_{16}^6$ and $A_{17}^7$ originate from the stretching vibrations of the tightly bound Se-Se pairs in the rectangular Se$_4$ unit. As shown in Figure 2a, the Raman-active modes other than $A_{16}^6$ and $A_{17}^7$ are all shifted towards larger wave numbers, which indicates an overall compression of the local lattice by the applied pressure. In contrast to the blueshift of other modes, both $A_{16}^6$ and $A_{17}^7$ exhibit a redshift upon initial compression, which was also observed in our simultaneous Raman scattering measurement with a configuration of $E_i \perp c$ (see Figure S3 and S4, Supporting Information). The redshift is generally indicative of a lattice instability, and in our case can be directly correlated to the displacements/rearrangements of Se-Se pairs in the Se$_4$ rectangles.

In contrast to the continuous redshift of $A_{16}^6$, $A_{17}^7$ demonstrates a crossover from redshift to blueshift at ca. 8 GPa (Figure 2b). Consistent with the pressure dependence of $d_{\text{intra}}$ (Figure 1d), the blueshift of $A_{17}^7$ suggests that the contraction of the chain diameter starts to manifest above ca. 8 GPa. Under higher pressures, the chain diameter is efficiently reduced, while the rectangular Se$_4$ unit continues to be instable, as revealed by the redshift of $A_{16}^6$. The interplay between these two mechanisms can effectively increase the degree of local disorder, and thus finally lead to the random distribution of the Se atoms in the atomic chains.

The linear chain compound shows an insulating behavior under low pressures, as evidenced by the increase of the thermoresistance, $R(T)$, by orders of magnitude at low temperatures (Figure 3a). Upon further compression, the increase of $R(T)$ is diminished, indicating the emergence of a dirty metallic state close to 20 GPa. Strikingly, above 20 GPa $R(T)$ starts demonstrating a resistive superconducting transition at low temperatures. We note that the emergence of the transition takes
place under the same pressure as that of the occurrence of amorphization in the TaSe$_4$ chains. This phenomenon is highly counterintuitive and intriguing, because in principle, a local lattice distortion, e.g., the pressure-induced short-range disorder in our case, should hinder Cooper pairing and set obstacles for the quantum condensation of Cooper pairs.$^{[32]}$ Superconductor-insulator transitions have been extensively studied for decades in a large variety of materials, where disorder serves as the driving force of the transition.$^{[33]}$ Opposite to the common cases, Figure 3a suggests that the insulator-superconductor transition observed in our quasi-1D system is facilitated by the amorphization of the TaSe$_4$ chains. Moreover, when increasing the applied pressure, the kink in $R(T)$ at ca. 260 K shifts towards lower temperatures and smears out at ca. 10 GPa (Figure 3a). This scenario suggests that the compression-induced disorder destroys the perfection of Fermi surface nesting and suppresses the CDW.$^{[34, 35]}$

As shown in Figure 3b, the resistive superconducting transition demonstrates an anomalous two-step feature with $T_1$ and $T_2$ being the onset critical temperatures of the two steps, respectively. To gain insight into the two-step resistive superconducting transition, we measured $R(T)$ in different magnetic fields, $\mu_0H$ (Figure 3c). When increasing $\mu_0H$, the two-step feature is shifted towards zero temperature and gradually smears out, along with the suppression of the superconducting state ($R = 0$). By tracking the magnetic field-induced evolution of $T_1$ and $T_2$, we build up the $\mu_0H-T$ phase diagram as shown in Figure 3d. Using the Werthammer-Helfand-Hohenberg (WHH) model,$^{[36]}$ we extrapolated the phase boundaries down to zero temperature. The extrapolation of the $\mu_0H-T_1$ phase boundary provides an estimation of the upper critical field of $\mu_0H_{c2}(0 \text{ K}) = 8.2$ T.

According to the Tomonaga–Luttinger liquid (TLL) theory, electron-electron interactions can be either repulsive or attractive in quasi-1D materials.$^{[37, 38]}$ In the case of attractive interactions, quasi-
1D superconductivity can emerge as a result of high-frequency intrachain bond vibrations. Apart from dimensionality, disorder acts as another key factor affecting electron-electron interactions. On one hand, it is commonly anticipated that disorder hinders superconductivity through amplification of the Coulomb repulsion between electrons. On the other hand, it has been revealed that disorder can lead to enhancement of phonon-mediated electron-electron attraction. Recently, disorder-enhanced superconductivity has been reported for a quasi-1D compound, Na$_{2-\delta}$Mo$_6$Se$_6$, where Na vacancies served as disorder centers. It was argued that the superconductivity was enhanced through disorder-correlated screening of Coulomb repulsion.

The existing theories raise intriguing questions about the dimensionality and origin of the superconductivity observed in our newly created quasi-1D system. In the case of 1D constriction, fluctuations of the superconducting order parameter, $\Psi$, can give rise to non-zero resistance below the bulk superconducting transition temperature. Along with the shrinkage of its amplitude down to zero, the phase of $\Psi$ slips by $2\pi$ at the so-called phase-slip centers. As shown in Figure 4, our observation of phase-slip behaviors indicates that the observed superconductivity in the lattice of amorphous atomic chains is highly likely quasi-1D. The intrachain Cooper pairing can be facilitated by disorder-correlated screening of Coulomb repulsion, as evidenced by the amorphization of the constituent atomic chains along with the emergence of superconductivity.

The emergence of superconductivity is further testified by the diamagnetization in ac susceptibility measurements (Figure 3e). The onset temperature of the diamagnetization, $T_s$, is plotted in Figure 5 as a function of the applied pressure. We note that in contrast to the electrical transport measurements which provide insight into the process of establishment of the percolation path for Cooper pairs, ac susceptibility measurements mainly reflect the formation of the circulating...
supercurrent.\textsuperscript{[45]} In the case of a disordered superconductor, local Cooper pairing sets in prior to the formation of the circulating supercurrent,\textsuperscript{[32, 45]} and thus the onset of superconductivity in electrical transports takes place at lower pressures (ca. 20 GPa) in contrast to the emergence of diamagnetization in ac susceptibility (ca. 30 GPa).

Based on the pressure-induced amorphization of the atomic chains and the emergence of superconductivity in our unconventional quasi-1D crystal, we build up the phase diagram as shown in Figure 5. Below ca. 20 GPa, the conventional quasi-1D crystalline phase is situated deep in the insulating regime. Upon the amorphization of the constituent atomic chains, the material is transformed into an unconventional quasi-1D system with long-range order but short-range disorder, and this newly created phase exhibits a two-step superconducting transition.

The \( T_1 - P \) and \( T_2 - P \) phase boundaries constructed through electrical transport measurements, divide the superconducting phase into two regimes, i.e., SC1 and SC2. Taking into account the quasi-1D nature of the system, we interpret SC1 as a result of the formation of precursor Cooper pairs localized inside the atomic chains. The intrachain Cooper pairing is followed by the interchain coupling via proximity effect, which gives rise to SC2 and the global superconducting state \( R = 0 \).\textsuperscript{[32]}

Our interpretation of the two-step resistive superconducting transition is consistent with the \( T_2 - P \) phase boundary lying below the \( T_2 - P \) phase boundary, because the Meissner expulsion only takes place when a percolation path is established for the circulation of supercurrent.\textsuperscript{[45]}

In conclusion, by compressing the quasi-1D material \((\text{TaSe}_4)_2\text{I}\), we created a new solid-state phase with the combination of long-range ordered and short-range disordered structures, which enriches the existing categories of solid-state materials. Furthermore, our data reveal that the
emergence of superconductivity in the linear chain crystal is highly correlated with the amorphization of its building blocks. This counterintuitive observation brings attention to the formation and quantum condensation of Cooper pairs in the presence of disorder at the atomic scale and low dimensionality. The constituent atomic chains of our newly created superconducting quasi-1D system can open up new perspectives in quantum electronics.

Experimental Section

Synthesis of the starting material: The \((\text{TaSe}_4)_2\text{I}\) single crystals were synthesized with chemical vapor transport (CVT) method. \[^3\]\] Stoichiometric Ta, Se powders and I\(_2\) pieces were ground together and loaded into a quartz tube. The tube was sealed in vacuum and placed in a two-zone furnace. The hot zone was maintained at 500 °C for two weeks, and the cold zone was maintained at 400 °C. Needle-shaped crystals were obtained on the cold end.

Synchrotron XRD measurements: High-pressure synchrotron XRD measurements with a beam wavelength of \(\lambda = 0.4133\ \text{Å}\) were performed at room temperature at the beamline of 16 BM-D, HPCAT of the Advanced Photon Source, \[^46\]\] Argonne National Laboratory. Daphne 7373 oil was used as the pressure transmitting medium. The DIOPTAS program was used for image integrations. \[^47\]\] The standard Rietveld method was used to fit the XRD patterns with the GSAS program. \[^48\]\] The ruby fluorescence method was used to determine the applied pressure. \[^49\]\]

Raman scattering measurements: High-pressure Raman scattering measurements on freshly cleaved \((\text{TaSe}_4)_2\text{I}\) single crystals were performed at room temperature using a solid-state laser (532 nm) for the excitation. The pressure was generated by a Mao-Bell-type symmetric DAC. Daphne 7373 oil was used.
used as the pressure transmitting medium. The ruby fluorescence method was used to determine the applied pressure at room temperature.\[^{[49]}\] The sample inside the cell was cleaved from a thin plate-like single crystal along the (110) natural cleavage plane and then cut into a rectangular bar with its long side along the c axis. The laser power was kept below 5% (2.5mW) to avoid sample damage and any heating effect. The Raman spectroscopy was measured in two configurations by aligning the polarization (\(E_i\)) of the incident laser parallel and perpendicular to the c axis, respectively. The frequency ranges from 50 to 400 cm\(^{-1}\).

**Electrical transport and ac susceptibility measurements:** The high-pressure electrical transport and ac susceptibility were measured by packing the sample in a screw-pressure-type diamond anvil cell (DAC) made of nonmagnetic Be-Cu alloy. The diamond culet was 300 \(\mu\)m in diameter. Sodium chloride (NaCl) powders were used as the pressure transmitting medium. Platinum foils with a thickness of 10 \(\mu\)m were used for the electrodes, and the standard four-probe method was used to characterize the electrical transport properties by sending the current along the c-axis. The ac susceptibility measurements were conducted using home-made coils that were wound around the diamond anvil. No pressure medium was used in the high-pressure magnetic measurements.

**Supporting Information**

Supporting information is available from the Wiley Online Library or from the author.

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Figure 1. Pressure-induced structural evolution of quasi-1D (TaSe₄)₂I as measured by synchrotron XRD. a) Schematic illustrations of the crystal structure of (TaSe₄)₂I projected in the a-b plane (left) and along the c axis (right). b) Room-temperature synchrotron XRD patterns measured under different pressures with an X-ray wavelength of λ = 0.4133 Å. c) Pressure dependence of the lattice parameters a and c. d) Pressure dependence of the interchain distance, $d_{\text{inter}} = a/\sqrt{2}$, and the diameter of the TaSe₄ chains, $d_{\text{intra}}$. The red dashed line is a linear fit of $d_{\text{intra}}$ above 8 GPa. e) Pressure-induced changes of $d_{\text{inter}}/d_{\text{intra}}$. 
Figure 2. Pressure-induced evolution of the local lattice symmetry as revealed by Raman scattering measurements. a) Raman spectra measured under different pressures in the configuration of $E_i//c$. The Raman-active modes, $A_{16}^i$ and $A_{17}^i$, are related to the vibrations of Se atoms. The blue circles show the pressure-induced redshift of $A_{16}^i$, and the magenta diamonds indicate the crossover from redshift to blueshift of $A_{17}^i$ at ca. 8 GPa. b) The Lorentzian line-shape fitting of $A_{16}^i$ and $A_{17}^i$ modes at 1.2 GPa (upper panel) and the pressure-induced evolution of $A_{16}^i$ and $A_{17}^i$ (bottom panel). The redshift of $A_{16}^i$ and $A_{17}^i$ below 8 GPa, redshift of $A_{16}^i$ (blueshift of $A_{17}^i$) between 8 and 18.1 GPa, and vanishment of Raman modes above 18.1 GPa, are highlighted in light blue, red and yellow, respectively.
Figure 3. Emergence of superconductivity in the quasi-1D system with amorphous constituent atomic chains. a) Thermoresistance, $R(T)$, measured under different pressures. Upon the amorphization of the constituent atomic chains at ca. 20 GPa, the system starts demonstrating a resistive superconducting transition. b) The anomalous two-step superconducting transition observed under high pressures. The onset critical temperatures of the two steps, $T_1$ and $T_2$, are indicated by arrows. c) Suppression of the two-step superconducting transition with different magnetic fields. d) Magnetic field dependences of $T_1$ and $T_2$. The $\mu_0 H - T_1$ and $\mu_0 H - T_2$ phase boundaries are extrapolated down to zero temperature using the WHH model (red curves) e) Superconductivity observed in ac susceptibility measurements under high pressures.
Figure 4. Phase-slip behaviors of the quasi-1D system with amorphous constituent atomic chains. a) Voltage versus current, $V(I)$, measured at different temperatures close to the offset superconducting transition temperature. b) $V(I)$ measured in different magnetic fields. c) and d) Magnetifications of the low-voltage regime of a) and b), respectively.
Figure 5. Temperature-pressure phase diagram. Above ca. 20 GPa, the insulating linear chain compound is transformed into a superconducting quasi-1D system made up of long-ranged ordered amorphous atomic chains. The $T$-$P$ phase boundaries divide the superconducting phase into two regimes, i.e., intrachain Cooper pairing (SC1) and interchain coupling (SC2).
Combination of long-range ordered and short-range disordered structures at the atomic level is demonstrated for a quasi-one-dimensional linear chain compound. Under compression, the constituent atomic chains of the material are amorphized without breaking the orientational and periodic translation symmetries of the chain lattice. This lattice of amorphous atomic chains hosts a quantum condensate of Cooper pairs.

**Combination of crystalline and amorphous structures**

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