Reentrant superconductivity in superatomic crystal $\text{AuTe}_2\text{Se}_{4/3}$
induced by pressure

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Abstract:
Superatomic crystal is a class of hierarchical materials composed of atomically precise clusters, self-assembling via van der Waals or covalent-like interactions. Here, we use the case of $\text{AuTe}_2\text{Se}_{4/3}$ to investigate the tunability of bonding strength and its impact on physical attributes on a superatomic level. We discover a pressure-mediated bonding-nonbonding transition, which switches the electronic conduction channel and alters the conductivity by three orders of magnitude. The initial superconductivity is quickly suppressed under pressure, but is followed by a secondary superconducting phase with a three-fold enhancement in the transition temperature ($T_c$). Combined with experimental and theoretical analyses, we established that reentrant superconductivity is triggered by the channel switching, which in turn has an intimate relationship with the recently found charge density wave (CDW) at a mesostructure scale.

Introduction- Interatomic interactions such as van der Waals (vdW) force, ionic, covalent and metallic bonds endow atomic solids a wealth of physics. $^{1,2}$ The mesoscopic analogue of atomic solid, coined as ‘superatomic crystal’, is made up of strong-bonded atomic clusters connected by weak interactions or covalent-like quasi-bonding (CLQB).$^3$ These superatomic clusters, on the other hand, behave collectively as conventional atoms with s-like, p-like, or d-like orbitals. Existing superatoms include fullerenes,$^4$ Zintl ions,$^5$ clusters of aluminum, silicon, boron, and metal chalcogenide molecular clusters. Hierarchical design of the superatomic building blocks and their subsequent stacking sequence provides an additional dimension to synthesize novel materials and discover emergent properties.$^6$

Although the existence of superatoms has long been recognized, the researches on superatomic crystals are burgeoning only recently. The major challenge lies in tailoring these clusters into crystals and probing how inter-cluster interaction affect their properties. The conductivity can be greatly altered by varying the mixture of different superatom species.$^7$ Several other properties such as photoluminescence and
The majority of the discovered superatomic crystals are diamagnetic semiconductors or insulators. Thus far, the mediation of the bonding strength and materials species mainly relies on self-assembling through organic capping ligands. The use of external tuning parameters to control and manipulate the inter-superatomic interactions remain an uncharted territory.

Only a handful of all-inorganic superatomic crystals have been reported. The newly discovered AuTe₂Se₄/3 (Fig. 1) is composed of cubic clusters with a precise chemical composition of Au₆Te₁₂Se₈. These 0D building blocks are woven together by anisotropic CLQB into 2D sheets and finally stacking along the c axis through vdW interaction. The shadow dotted lines between superatoms shown in Fig. 1 represent bundles of Te-Te bonds as a characteristic parameter, while the cube itself can be considered a rigid body. This material was initially discovered in our lab and later reported to be a natural mineral found in the Koryak Highlands (Russia). To the best of our knowledge, AuTe₂Se₄/3 is the first all-inorganic superatomic superconductor.

High-pressure measurement, as a clean and feasible external tuning knob, has been widely used in the realm of atomic solids and quantum materials. In this Letter, we explore the possibility of tuning and controlling bond strength at the superatomic level by pressure. We substantiate that the superatomic cubes remain intact but experience a systematic glide. Concomitantly, a pressure-driven nonbonding-bonding transition between cubes is observed, which has a major impact on both the anisotropic transport properties and superconductivity. Combined with experimental and theoretical analysis, we discuss the intimate relationship between the observed reentrant superconductivity and the S-CDW order.

FIG. 1. Structural heterogeneity of superatomic crystal AuTe₂Se₄/3. (a) Each van der Waals (vdW) layer is composed of arrays of superatoms connected by covalent-like quasi-bonds (b). (c) Atomically precise cubic with a composition of Au₆Te₁₂Se₈.
Experimental- Single crystalline AuTe$_2$Se$_{4/3}$ was grown using the self-flux method as described in reference 12. In-situ high pressure electrical transport of AuTe$_2$Se$_{4/3}$ single crystal was measured in a physical property measurement system (PPMS, Quantum Design) by using a diamond anvil cell (DAC) with the facet diameter of 300 nm. We used the van der Pauw method to measure the electrical transport properties. The cubic boron nitride (cBN) powders were employed as pressure transmitting medium and insulating material. Before and after each measurement, the pressure was measured using the ruby fluorescence method at room temperature. In-situ high pressure Raman spectra (Horiba, Lab-RAM HR revolution) were taken at room temperature.

Theoretical calculations- Structural relaxation and electronic calculations were performed using density functional theory within Perdew-Burke-Ernzerh (PBE)\textsuperscript{16} of exchange-correlation and generalized gradient approximation (GGA) functional as implemented in Vienna \textit{ab-initio} Simulation Package (VASP) code.\textsuperscript{17} The lattice parameters and atomic positions were fully relaxed without any symmetry constraints. All electron projector-augmented wave approach was adopted with the plane-wave cutoffs of 500 eV and Monkhorst-Pack\textsuperscript{18} $k$-meshes with a grid spacing of $2\pi \times 0.02$ Å$^{-1}$ were used to achieve a good convergence for the enthalpy.

Results and discussion- Four types of Te-Te interactions can be recognized based on the relative positions of the superatomic cubes, as shown in Fig. 2 and Fig. S1. We trace the evolution of bond length under pressure. The longest Te-Te bond, according to the Ref.19, is 3.8 Å, over which the pair is considered non-bonding. Since the contribution of Se-Se and Se-Te to DOS is negligible at the Fermi level (Fig. S6), we employ Te-Te bonds as criteria for the inter-superatomic CLQB along different spatial directions. At ambient pressure, Te(1) belongs to a type of strong CLQB that forms a 1D chain along the a-axis (Fig. S13). Te(2) bond is a weak CLQB that locates at the boundary of bonding-nonbonding crossover and interwoven the 1D chains to form a quasi-2D plane. Te(3) and Te(4) are pressure-induced CLQBs, approximately pointing along the direction of $b$- and $c$- axes, respectively.

As illustrated in Fig. 2a, Te(1) and Te(2) initially decrease with the increase of pressure and jump to larger values within 5-10 GPa, but remain in the bonding region. At the same critical pressure, Te(3) and Te(4) go through a nonbonding-bonding transition, implying an abrupt lattice transformation. At 10 GPa, we discovered that Te(3) and Te(4) show lower values than that of Te(1) and Te(2), indicating the generation of stronger CLQBs along the $b$- and $c$-axes. We further use pressure-dependent x-ray diffractions (wavelength $\lambda = 0.7107$ Å) to confirm the predicted structural transition. The experimental data are shown in Figure 2b, together with simulated diffraction patterns (green curves) at 10 GPa and ambient pressure. The significant difference between before and after the crystal glide is the appearance of appreciable diffraction peaks at around 21-23 degrees (red arrow). The superimposed red solid curves are refinement results using the calculated crystal structures, which show a perfect match to the experimental data. Our Raman measurements back up this pressure-driven nonbonding-
bonding transition. The identical Raman pattern after releasing pressure (Fig. S3) to the original one confirms that AuTe$_2$Se$_{4/3}$ does not decompose during measurement. At 5 GPa, a small peak at 163.5 cm$^{-1}$ appears as the pressure rises. This matches our theoretical prediction of Te(3) and Te(4) formation, one of which may contribute to the additional vibration mode. The variation of Te-Te bond lengths, angles and lattice constants from 0 to 60 GPa can be found in Fig. S2.

FIG. 2. 2D-3D evolution of superatomic crystal AuTe$_2$Se$_{4/3}$ under external pressure. (a) Pressure-dependent of four kinds of Te-Te distances. (b) X-ray diffraction ($\lambda = 0.7107$ Å) patterns of AuTe$_2$Se$_{4/3}$ at 9.1 GPa and ambient pressure. The green curves are simulated diffraction patterns based on predicted structural models at 10 and 0 GPa. (c,d) Comparison of the structure change at ambient pressure and 10 GPa. A systematic gliding of the superatomic array along the b axis is illustrated with the reference of its initial position depicted in gray dashed squares. Figure S1 shows another crystal gliding along a axis. Bonds formation along each crystalline axis is painted in color with the reference to (a). We use Te(1) as a shorthand for Te-Te(1) bond and the same goes for other bonds.

To visualize the aforementioned nonbonding-bonding transition, we calculate the valence electron location function (ELF) in Fig. S6. The values of 0.5 and 1 are the indicators of covalent and ionic bonds, respectively. Because the Se is more electronegative than that of Te, Au-$d$ electrons incline to transfer to Se atoms, and their contributions are mainly confined inside the cube. There are many electrons localized between Te and Se atoms in a single Au$_6$Te$_{12}$Se$_8$ cube with comparable ELF values at around 0.6, much higher than that of 0.11 in between cubes, indicating the robustness
of the superatoms under pressure. At ambient pressure, the inter-cubic Te-Te interaction is along the \( a \)-axis. At \( P = 10 \) GPa, however, electrons are confined between inter-cubic Te-Te bonds along the \( b \)-axis. Charge redistribution within distinct crystal directions is caused by these pressure-induced CLQBs.

The pressure-driven nonbonding-bonding transition should be reflected in anisotropic transport properties. Figure 3a and Figures S7-S9 show the pressure-dependent \( \rho_c/\rho_a \). The electrode layout is shown in the inset. The \( \rho_c/\rho_a \) ratio changes from 11 to \( \sim 0.05 \) when the external pressure is increased from 0.8 to 40 GPa. This ratio decreases dramatically at low pressure and progressively saturates at high pressure, qualitatively agreeing with the trend of Te(3) and Te(4) bond lengths. Since the DAC measurements cannot guarantee a perfect hydrostatic pressure condition, sample deformation may also cause a drop in \( \rho_c/\rho_a \). For a compact single crystal, however, the general geometric deformation \( \Delta l_c/\Delta l_a \) should be smaller than 2. (judging from the sample size before and after measurements). The observed decrement of \( \rho_c/\rho_a \) by three orders of magnitude reflects the intrinsic bonding evolution. An interesting observation is the \( \rho_c/\rho_a = 1 \) in the pressure at around 7 GPa, agreeing well with the calculated bond evolution. Given the nearly identical behavior of Te(3) and Te(4) bonds shown in Fig. 2(a), we infer that \( \rho_b/\rho_a \) should follow a similar pattern. From the above analyses, we propose a CLQB-driven switching of the electrical conducting channels from the \( a \)-axis to \( b \)- and \( c \)-axes.

FIG. 3. Reentrant superconductivity in superatomic crystal \( \text{AuTe}_2\text{Se}_{4/3} \) under external pressure. (a) A logarithmic plot of anisotropic resistance ratio \( \rho_c/\rho_a \) as a function of
pressure increment. Inset shows the electrode layout along the c-axis (blue) and within ab plane (magenta) (b) Temperature-dependent resistivity at low-pressure region (0.8-5.3 GPa). Inset is the superconducting transition at ambient pressure. (c) $\rho$-$T$ curves at a high-pressure region (6.6-59.7 GPa). Reentrance of superconductivity can be observed accompanied by the monotonic increment of normal state resistivity (cyan arrow). The transition temperature ($T_c$) is determined by the derivative of the $\rho$-$T$ curves, as shown in the inset. These peak values are summarized in a unified phase diagram(d).

This channel switching generates a profound influence on its superconductivity. As shown in Fig. 3b-c and Fig. S10-S11, the initial superconducting transition is quickly suppressed by pressure and cannot be observed at 1.3 GPa above 2 K. In accordance with the upturn of the Te(1) bond (Fig. 2a), the normal state resistivity first declines and then monotonically increases with a transition point at 6.6 GPa. Accompanied by the upturn, we observe reemergent superconductivity with a sharp transition to zero resistance. The highest $T_c$ reaches 8.5 K at 60 GPa, which is three times higher than the initial $T_c$ of 2.8 K at ambient pressure. The $\rho$-$T$ curves of the reentrant superconductivity under various magnetic fields are shown in Fig. S12, from which we derive its $H_{c2} = 3.5$ T. Figure 3d depicts the evolution of $T_c$ under external pressure. A second superconducting dome can be observed, with a significantly higher $T_c$. Although reentrant superconductivity has been discovered in a variety of compounds, including K$_x$Fe$_{2-y}$Se$_2$ and CsV$_3$Sb$_5$,21,22 this is the first time it has been observed in a superatomic crystal system by tuning CLQBs.

![FIG. 4. Band and Fermi surface evolution of AuTe$_2$Se$_{4/3}$ under external pressure. (a,b) Partial projection of band structures of AuTe$_2$Se$_{4/3}$ at ambient pressure and 10 GPa. (c) The Fermi surface at ambient pressure consists of one quasi 2D sheet generated by band](image-url)
#1, one small cylindrical electron surface by band #5, and three quasi-1D plate-like sheets by bands #2, band #3, and band #4. (d) Deformed Fermi surface topology of bands from #1 to #5 under an external pressure of 10 GPa.

Figures 4a and 4b display the pressure-dependent projected band structure. At ambient condition, the Au-\(d\) component (omitted for clarity) mainly hybridizes with Te-\(p_x\) orbitals around the Fermi level (\(E_F\)), forming the flat bands along \(\Gamma\rightarrow F\rightarrow Q\rightarrow Z\rightarrow \Gamma\). The strong electronic localization behavior and the highly dispersed Te-\(p_x\) bands (#2, #3, and #4 in Fig. 4c) along \(\Gamma\rightarrow B\) path are in agreement with the quasi-1D structure along the \(a\)-axis and the previous ARPES studies. Meanwhile, multiple 3D Te-Te CLQBs form at \(P = 10\) GPa, resulting in larger dispersive bands around the \(E_F\) and higher Fermi velocity. In the percentage of the density of states plot (PDOS, Fig. S13-S14) for AuTe\(_2\)Se\(_{4/3}\), the Te-\(p\) orbital dominates the \(E_F\) and is responsible for their metallicity. When the pressure is raised to 10 GPa, the main contribution at the \(E_F\) shifts from Te-\(p_x\) to Te-\(p_y\), which corresponds to the creation of Te(3) CLQB along the \(b\)-axis. We also notice the contribution of Te-\(p_y\) orbitals becomes maximal when AuTe\(_2\)Se\(_{4/3}\) reentrants superconductivity. These findings show that the interplay between the different orbital electrons is responsible for the emergence of the second superconducting dome. The decrease in carrier concentration owing to the creation of CLQBs is likewise consistent with the abrupt drop in PDOS from 5 to 10 GPa (Fig. S15). Meanwhile, overall DOS values drop from 4.61 to 2.63 states/eV, then rise to 4.77 states/eV (Fig. S14), which is qualitatively consistent with pressure-dependent \(T_c\) change.

We plot the pressure-dependent Fermi surface of AuTe\(_2\)Se\(_{4/3}\) in Fig. 4c-d and Fig. S16. The topology of Fermi surface gradually evolves into three dimensions under pressure. Note that there are two essential aspects of change at \(P=10\) GPa. First, the quasi-2D band #1 deforms into four adjacent 3D Fermi surfaces. The quasi-1D surfaces of band #3 and band #4 become two quasi-2D corrugated cylinders. Second, the three Fermi surfaces of bands #2, #3, and #4 rotate by 90 degrees, indicating that the direction of electron flow shifts from \(a\)-axis to \(b\)-axis. These results strongly support our suggested pressure-driven 2D-3D crossover and conduction channel switching.

**Discussion and conclusion**—Very recently STM and ARPES measurements revealed a spontaneous electronic polarization within each Au\(_6\)Te\(_{12}\)Se\(_8\) cube, which collectively forms a triple-cube-width stripe period along the \(b\)-axis. The concomitant reentrant superconductivity and the CLQB formation along the \(b\)-axis suggests that the second superconducting phase and the S-CDW are inextricably linked. Superconductivity and CDW, as two kinds of electronic ground states, their competition and collaboration behavior have been extensively investigated in numerous atomic compounds, including IrTe\(_2\), ZrTe\(_3\), and CsV\(_3\)Sb\(_5\). The observation of S-CDW in AuTe\(_2\)Se\(_{4/3}\) provides a unique opportunity to investigate the mutual interaction of the two distinct superconducting phases and CDW at a mesostructure level. We will not tackle this issue
here, for one thing, the DAC measurement is not suitable for fine-tuning in the low-pressure region, for another the S-CDW signal cannot be clearly distinguished from our resistivity measurements. Novel methods with high pressure and CDW-sensitive detection capability are highly desired.

The hierarchy of matter structures corresponds to distinct energy scales and induces emergent physical phenomena. Superatomic structures, with inner unit clusters and pseudo-orbitals, behave collectively as an atomic assembly at mesoscopic levels. Because the relative closeness of the energy scales between inter-CLQB and intra-ionic bonds, the superatomic crystal may serve as a model system to investigate emergent phenomena with ease. For instance, the inner atomic clusters of AuTe$_2$Se$_{4/3}$ may begin to change a higher pressure (> 60 GPa). Novel critical behaviors and strong correlations between clusters will emerge.

In summary, we successfully incorporate external high pressure as a degree of freedom into superatomic crystal, using AuTe$_2$Se$_{4/3}$ as an example. The rigid superatomic building blocks go through a crystal glide at a critical pressure point, causing a nonbonding-bonding transition. As a result, the anisotropic ratio changed by three orders of magnitude, as evidenced by our theoretical calculation of Fermi surface rotation by 90 degrees. Remarkably, we observe reentrance of superconductivity triggered by the channel switching with a threefold increase in $T_c$. The close connection between superconductivity and the recently discovered superatomic-CDW order merits further exploration. We anticipate this work will boost the hierarchical design and assembly of novel superatomic superconductors, as well as give a potential technique for modifying exceptional physical features in superatomic crystals that have already been identified and beyond.

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**References**
1. T. Yokoya, et al. Fermi surface sheet-dependent superconductivity in 2H-NbSe$_2$. *Science* **294**, 2518 (2001).
2. D. Xiao, et al. Coupled spin and valley physics in monolayers of MoS$_2$ and other group-VI dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).
3. E. A. Doud, et al. Superatoms in materials science. *Nat. Rev. Mater.* **5**, 371 (2020).
4. A. Canning, G. Galli, and J. Kim. Carbon superatom thin films. *Phys. Rev. Lett.* **78**, 4442 (1997).
5. F. Pan, B. Weinert, and S. Dehnen. Binary Zintl anions involving group 13–15 (Semi-) metal atoms, and the relationship of their structures to electron count. *Structure and Bonding* **15**, 1 (2021).
6. W. Xie, et al. Magnetic coupling induced self-assembly at atomic level. *Chinese Phys. Lett.* **36**, 116401 (2019).
7. X. Cui, et al. Realizing nearly-free-electron like conduction band in a molecular film through mediating intermolecular van der waals interactions. *Nat. Commun.* **10**, 3374 (2019).
8. J. Yang, et al. Superatomic solid solutions. *Nat. Chem.* **13**, 607 (2021).
9. A. Voevodin, et al. Multifunctional vesicles from a self-assembled cluster-containing diblock copolymer. *J. Am. Chem. Soc.* **140**, 5607 (2018).
10. C. Fischer, et al. Crystal structure and thermodynamic analysis of the new semiconducting chevrel phase Re$_2$S$_2$Cl$_2$. *Berichte Der Bunsengesellschaft Für Phys. Chemie* **96**, 1652 (1992).
11. N. L. Speziali, et al. Single crystal growth, structure and characterization of the octahedral cluster compound Re$_2$Se$_6$Br$_2$. *Mat. Res. Bull.*, **23**, 1597 (1988).
12. J. G. Guo, et al. Quasi-two-dimensional superconductivity from dimerization of atomically ordered AuTe$_2$Se$_{4/3}$ cubes. *Nat. Commun.* **8**, 871 (2017).
13. X. Y. Jia, et al. Nodeless superconductivity in a quasi-two-dimensional superconductor AuTe$_2$Se$_{4/3}$. *Chin. Phys. B* **27**, 067401 (2018).
14. N. D. Tolstykh, et al. Maletoyvayamite, Au$_3$Se$_4$Te$_6$, a new mineral from Maletoyvayam deposit, Kamchatka peninsula, Russia. *Mineral. Mag.* **84**, 117 (2020).
15. S. Y. Xing, et al. Emerging correlated charge orders in a layered super-atomic crystal. Arxiv: 2110.09058 (2021).
16. J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
17. G. Kresse and J. Furthmüller, Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15 (1996).
18. H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188 (1976).
19. https://www.powells.com/book/crc-handbook-of-chemistry-physics-81st-edition-9780849304811.
20. Y. Ma, et al. Transparent dense sodium. *Nature* **457**, 182 (2009).
21. L. L. Sun, et al. Re-emerging superconductivity at 48 kelvin in iron chalcogenides. *Nature* **483**, 67 (2012).
22. X. Chen, et al. Highly robust reentrant superconductivity in CsV$_3$Sb$_5$ under Pressure. *Chinese Phys. Lett.* **38**, 057402 (2021).
23. Y. S. Oh, et al. P Anionic Depolymerization transition in IrTe$_2$. *Phys. Rev. Lett.* **110**, 127209 (2013).
24. R. Yomo, et al. Pressure effect on competition between charge density wave and superconductivity in ZrTe$_3$: Appearance of pressure-induced reentrant superconductivity. *Phys. Rev.*
K. Y. Chen, et al. Double superconducting dome and triple enhancement of $T_c$ in the Kagome superconductor CsV$_3$Sb$_5$ under high pressure. Phys. Rev. lett. 71, 1247001 (2021).