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Discovery of New Metallic and Superconducting Phase in GaTa_4Se_8 Under High Pressure

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Pressure is a unique thermodynamic variable to explore the phase competitions and novel phases inaccessible at ambient conditions. The resistive switching material GaTa_4Se_8 displays several quantum phases under pressure, such as $J_{\text{eff}} = 3/2$ Mott insulator, correlated quantum magnetic metal, and d-wave topological superconductivity, which has recently drawn mounting interest. Using high-pressure Raman, X-ray diffraction, extended X-ray absorption, and transport measurements, together with theoretical calculations, we reveal a remarkably rich phase diagram of this molecular magnetic Mott insulator at pressures up to ~ 68 GPa. In this previously unreachable pressure regime, we find, GaTa_4Se_8 exhibits a new metallic phase whose structural and magnetic properties are clearly distinctive from the lower pressure one. Further, we identify a new superconducting phase in this high-pressure regime below $T_c \sim 5.5\text{K}$. Our discoveries highlight GaTa_4Se_8 as a unique playground in which novel quantum phases and orders coexist and compete with each other; ranges from Mott insulator to Fermi liquid and exhibits multiple metallic and superconducting states.

External control of conductivity is one of the most promising schemes for realizing energy-efficient electronic devices. It essentially relies on a detailed understanding of the insulator-metal transition (IMT)¹⁻³. Unveiling the driving mechanism behind the IMT in electron correlated materials and the various phenomena in the vicinity of it represents one of the longest-standing enigmas in condensed matter physics^{4,5}. Exotic physical properties including quantum magnetism and unconventional superconductivity often arise around this transition. Many physical ingredients compete with and against each other such as electron-electron, electron-lattice and spin-orbit interactions. Among such materials, solid molecular GaTa₄Se₈ (GTS), a candidate for resistive switching materials and memory devices, is unique in that its IMT has no concomitant structural transition and no long-range magnetic ordering observed⁶⁻¹⁴.

GTS is commonly described as a deficient spinel with a symmetry of $F\bar{4}3m$. Tantalum atoms are shifted off the Se octahedral cage centers forming tetrahedral Ta₄Se₄- (or Ta₄-) clusters with the intra-cluster Ta-Ta distances of $< 3 \text{ \AA}$ and the inter-cluster distances of $> 4 \text{ \AA}$. GTS remains in a cubic and insulating phase down to the lowest temperatures with no concurring structural transition. In contrast, most of the other lacunar spinels' insulating states are stable in a slightly distorted cubic lattice (i.e. rhombohedral lattice) and magnetically ordered phase^{13,15,16}. Although GTS has long been known as paramagnetic¹¹ down to low temperature, its magnetic property has recently drawn much attention after the theoretical and experimental reports of a so-called molecular $J_{eff} = 3/2$ moment residing in this material¹⁷⁻¹⁹. This novel magnetic ground state is a concerted result of triply-degenerated t_2 molecular orbitals and strong spin-orbit coupling (SOC). By applying pressure, GTS exhibits successive transitions from Mott insulator to metal and metal to superconductor¹¹. In addition to its unique magnetic and transport properties at the

ambient conditions, the phases that can arise in this material include topological *d*-wave superconductivity²⁰, correlated $J_{eff} = 3/2$ metal¹⁹, spin-freezing superconductivity¹⁹ and a multipolar magnetic phase²¹. However, such vast and exciting possibilities have largely remained unexplored, especially in the high-pressure regime.

Here, we systematically investigated GTS' structural, electronic, and magnetic properties up to a high pressure that has not been reached before. We identified two metallic phases in a monoclinic symmetry by combining Raman spectroscopy and extended X-ray absorption spectroscopy (EXAFS) together with X-ray diffraction (XRD) and transport measurement up to ~ 68 GPa. Further, we observed a clear superconductivity signature at pressures above ~ 40 GPa in the second metallic phase. Our theoretical calculations indicate that both these high-pressure metallic and superconducting phases are distinctive from those previously reported in a lower pressure range¹¹. Thus, we were able to construct an extended P - T phase diagram for GTS, identifying new structural, magnetic transitions, and superconductivity. Our findings render GTS a unique example that hosts unusually rich physical phases in a single material from a structural, metallicity, magnetism, and superconductivity perspective.

Low-pressure regime ($P < 8$ GPa): insulating phase

Figures 1(a), (b) and (c) display the results of our XRD, Raman and EXAFS experiments, respectively. No change could be resolved from XRD up to 8 GPa, which is consistent with previous reports^{11,13}. On the other hand, our Raman and EXAFS data indicate structural changes at around $P = 2$ -3 GPa. Figure 1(b) clearly shows that the Raman peak at about 250 cm^{-1} splits into two peaks (peak 1 and 2) in the pressure above ~ 3 GPa which were previously assigned as Ta-Se

stretching modes¹¹. It is reminiscent of the mode splitting accompanied by a structural distortion observed in GaV_4Se_8 ²².

This pressure-dependent structural mode change is also signaled in another traditional local probe EXAFS. Figure 1(c) is the radial distribution function obtained by the Fourier transformation of Ta L_2 -edge EXAFS data. The peak positions represent the inter-atomic distances although they are usually not equal to the real bond length due to the phase shift²³. The first, second, third, and fourth peaks correspond to the intra-cluster Ta-Se, Ta-Ta, and two inter-cluster Ta-Ta distances, respectively. Note that the widths of peak 2 at higher pressures deviate from the one at the lowest pressure of 0.7 GPa, indicating the symmetry lowering of the Ta_4Se_4 cluster.

Considering all the results from XRD, Raman and EXAFS together, we conclude that, besides the static lattice distortion at low temperature²¹, the Ta_4Se_4 cluster is also locally distorted into a lower symmetry at $P \geq 2\text{-}3$ GPa (however, the symmetry of the distorted cluster is unable to be resolved from our XRD). Interestingly, this pressure range is close to the previously-reported critical pressure of the IMT, $P_c \sim 3.5$ GPa, in a single-crystal sample¹². Thus, we suspect that this structural mode can possibly be related to an IMT by partly lifting the triple degeneracy of the t_2 molecular orbital levels although the IMT phase boundary exists in a higher pressure range in our experiment (see below).

Care must be taken when the critical value of P_c is determined from different experiments, especially, because of the following challenges in these types of measurements: (1) the experimental probes might not be sensitive enough to resolve subtle structure changes; and (2) the pressure commonly varies with temperature in high-pressure electrical resistance measurements, which introduces errors in determining the P_c . In our set-up, the resistance and Raman spectra were

simultaneously measured on the same sample and at the same pressure-temperature conditions to overcome these problems. Furthermore, the pressure was continuously recorded in the meantime every ~ 20 K during cooling or heating. This set-up can minimize the errors and therefore allow us to obtain a more reliable estimation of P_c . Hereafter, we explicitly denote two pressure values for each data set. They correspond to the lowest and the highest temperature through which we keep measuring the pressure.

Moderate-pressure regime ($P = 8\text{-}22$ GPa): weakly insulating or bad metallic phase

It is well known in GTS that applying further pressure results in a Mott insulator to metal transition. Figure 2(a)-(l) present our electrical resistance results at different pressures. In the low-pressure regime of $P \leq 4.5/10.2$ GPa (where 4.5 GPa is the pressure value measured at 300 K and 10.2 GPa is at 7 K), the resistance exhibits insulating behavior with temperature dependence.

In the pressure range above 8.4/14.7 GPa (at 300/7 K), the resistance value drops by about four orders of magnitude, e.g., from $10^6 \Omega$ at 0.8/5.0 GPa to 38Ω at 11.9/18.2 GPa. This behavior is retained in the pressure range from 8.4/14.7 GPa to 11.9/18.2 GPa and briefly also to 18.2/25.3 GPa (at 300/7 K). On the one hand, this phase is much more metal-like by having far smaller resistance than the Mott insulating phase. On the other hand, its temperature dependence is still insulator-like, showing an upturn at lower temperatures. Therefore, one can assign this phase as bad metallic or weakly insulating. The former seems to be the more consistent name with previous studies in the sense that our on-set pressure of this behavior, $P \sim 8.4/14.7$ GPa, is in a reasonable agreement with the previously reported critical pressure of IMT, $P_c \sim 15$ GPa, in a polycrystalline sample¹¹.

High-pressure regime ($P > 22$ GPa): two metallic and superconducting phases

Applying higher pressure eventually turns the resistance behavior to become clearly metallic. The charge gap Δ , which is obtained by linear fitting of data to $R(T) = e^{\Delta/2k_B T}$ vs $1/T$ where k_B is Boltzmann's constant, becomes zero at $\sim 22.0/29.6$ GPa (for more details and Raman data, see Supplementary Information). Figure 2(g)-(i) also shows that, at $P \geq 22.0/29.6$ GPa (at 300/7 K), the resistance decreases as the temperature is lowered and this trend persists up to 32.0/41.1 GPa. We name this metallic phase as 'Metal 1' to distinguish it from 'Metal 2', which appears in the even higher pressure (see below). Metal 1 most likely corresponds to the previously reported metallic phase in the pressure range higher than 15 GPa¹¹, or 6 GPa¹⁴, or 3.5 GPa¹². Simultaneously, we do not exclude the possibility that the lower pressure 'weakly insulating or bad metallic' phase in $P \sim 8.4/14.7$ -18.2/25.3 GPa was not clearly distinguished from Metal 1 in the previous experiments possibly because of the following reasons: i.e., the critical pressure value P_c is sensitive to the applied external voltage in resistance measurements⁶⁻¹⁰, as well as to the non-stoichiometry and grain size of samples, and the stress conditions in the high-pressure environments.

Importantly, structural data also signals the phase change upon entering into the Metal 1 region of pressure. The continuous softening of peak 2 in Figures 3(a)-(b) suggests the vibration mode of the Ta₄Se₄ cluster becomes increasingly unstable at high pressure, while the increased splitting between peak 1 and peak 2 indicates the Ta₄Se₄ cluster becomes more distorted under compression. These changes eventually trigger a structural transition. Figure 3(c) shows that a new XRD peak starts to be developed at $P = 23.4$ GPa (300 K; indicated by an arrow). It is also consistent with

the Raman spectra whose feature starts to become different at $P \geq 22.0$ GPa (at 300 K); see Fig. 3(a). The structure of Metal 1 as determined by our XRD (Figure 3(d)) has $C2$ symmetry. This new monoclinic metallic phase still inherits the similar Ta_4Se_4 clusters as a basic molecular unit and the cubic phase's topological configurations. However, it has a reduced inter-cluster distance and a more distorted Ta_4Se_4 cluster (see Supplementary Information for more details). This symmetry change in the crystal structure has not been identified in the previous studies¹¹⁻¹⁴.

Therefore, our finding suggests that the current understanding of the IMT in this material requires an update: the role of pressure is not only to increase the inter-cluster hopping and thus to reduce U/t value of Hubbard model^{11-14,19}, but it also lifts a part of degeneracy to assist the Mott transition, similar to the well-known Mott-Peierls type IMT in VO_2 . However, the IMT in VO_2 results in a metallic phase in a higher symmetry than its insulating phase, whereas the IMT in GTS results a metallic phase in a lower symmetry than its insulating phase. This suggests the driving force for the IMT in the two material systems are possibly different, thereby requiring further experimental and theoretical investigation in the future.

Metal 2 phase: Normal metal and superconductivity

Under even higher pressure, we observed more characteristic resistance behavior. Note that this pressure range has not been reached before in this material. For $P > 40.8/47.6$ GPa (at 300/7 K), the temperature-dependent resistance changes again while the resistance values themselves are gradually reduced. It is indicative of a new metallic phase arising at high enough pressure. As a result of this, we name this second metallic phase as 'Metal 2'. Remarkably, in this pressure regime of Metal 2, a superconducting transition is clearly observed by lowering the temperature. Figures

2(i)-(l) show the superconducting transition starts to appear above $P \sim 32.0/41.1$ GPa and is robustly observed up to the highest possible pressure of $P \sim 60.7/68.4$ GPa with superconductivity transition temperature (T_c) slightly decreasing from 5.6 to 5.2 K (see Figures 2(m)-(p)). The upper critical field for superconductivity is ~ 7 T (see Figure 2(q)). We do not find the superconductivity signal well inside the Metal 1 regime and the temperature range down to 5 K (see Supplementary Information for further discussion). As discussed further below, we presume that this high-pressure superconductivity is a different type from the one previously reported in the lower pressure range¹¹.

As a new phase, Metal 2 is of particular interest. In addition to the different transport behavior discussed above, Metal 2 exhibits several other distinctive features from Metal 1. First, its pressure range is obviously much higher than that of Metal 1. Compared to the IMT pressure reported by previous studies^{11,12,14}, the on-set pressure for Metal 2 is higher by ~ 25 -40 GPa. We believe that this is far beyond the experimental uncertainty. Second, Raman data also indicates a phase change. Figures 3(a, b) is the Raman spectra collected on the same sample during the electrical resistance measurements. We note that Raman modes well inside the Metal 2 regime ($P \geq 51.6/58.2$ GPa at 300/7 K) are markedly different from those of Metal 1. Third, our XRD data, albeit less clear, also exhibits a noticeable difference at $P \geq 44.9$ GPa (at 300K) from that of $P \leq 39.9$ GPa (at 300 K); see Fig. 3(c).

Finally, our theoretical calculations provide further insights on a distinctive Metal 2 phase to Metal 1. Figures 3(g) and (h) shows the band dispersion and the density of states (DOS), respectively, calculated with the structure obtained experimentally at $P \sim 50.2$ GPa. It clearly exhibits a metallic character. Importantly, we found that the electronic structure does not significantly change by including SOC, which is in a sharp contrast to the low-pressure situation;

see Fig. 3(g). In the low-pressure phases, the well-defined molecular $J_{eff} = 3/2$ and $1/2$ bands are clearly identified by taking SOC into account¹⁷⁻¹⁹. On the other hand, in this high-pressure regime, the molecular orbitals are not well defined and the projection onto the J_{eff} state fails, implying that this compound's molecular nature is no longer retained; see Fig. 3(h). In fact, the inter-cluster Ta-Ta distance (~ 3.3 - 4.0 Å) in this regime becomes comparable with the intra-cluster distance (~ 2.6 - 3.7 Å).

Another key difference is the magnetic property. Our calculation shows that the Metal 2 phase is non-magnetic. Further, we observe that calculations hardly converge to the magnetic solution even with a sizable U value assigned onto the Ta atoms within the DFT + U scheme. Given that DFT + U is such a method that highly overestimates the magnetic moment formation tendency, it is a strong evidence that Metal 2 is non-magnetic, and its ground state is far from the magnetic instability. Therefore, it is clearly different from the lower pressure metallic phases for which the well-defined $J_{eff} = 3/2$ moment is revealed by previous RIXS experiment, DFT + U , and DFT + DMFT calculations¹⁷⁻¹⁹.

Our further calculations of the electronic and magnetic characteristics suggest that Metal 2 is a conventional non-magnetic metal (for more discussion can be found in Supplementary Information). Accordingly, the superconductivity found in this pressure regime is most likely conventional BCS-type. Namely, not only a different type of metal but also a different superconducting phase are stabilized in this high-pressure regime, distinctive from the ones in the lower pressure. For the superconductivity derived from Metal 1, the previous study showed that it is unconventional d -wave topological type arising from correlated $J_{eff} = 3/2$ metallic bands²⁰.

Summary: extended phase diagram

Our results establish GTS as a unique material system in which Mott insulator, correlated $J_{eff} = 3/2$ metal¹⁹, and conventional metal phase successively arises as a function of pressure. A different type of superconductivity is also found at low temperatures. To summarize, Figure 4 displays the constructed P - T phase diagram. We found that the Mott insulator to metal transition concurs with a symmetry lowering structural transition from cubic to monoclinic, renewing our understanding of the IMT in this material at high pressure. The Metal 2 phase and the superconductivity derived from it have been discovered in the high-pressure regime. Our calculations indicate that the Metal 1-to-Metal 2 transition is presumably also accompanied with the magnetic transition; namely, from the recently reported $J_{eff} = 3/2$ metal¹⁹ to normal non-magnetic normal metal.

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Figure 1. The XRD, Raman spectroscopy, and EXAFS measurements on GTS in low-high pressure regime. The pressure values (unit: GPa) are printed close to each pattern. (a) XRD patterns were obtained from 0.8 to 8.0 GPa at 30 K, and no structural change is observed; (b) Raman spectra were collected from 0.4 to 10 GPa at room temperature. The peak 1 between 200 and 250 cm^{-1} that splits into two peaks appears at 4.2 GPa; (c) The EXFAS spectra are measured from 0.7 to 5.4 GPa at room temperature and significant broadening of the second peak 2 occurs above 1.9 GPa. The insets are the model of the Ta_4Se_4 clusters.

Figure 2. The plots of electrical resistance measurements ranging from 0.8/5.0 GPa to 61.4/68.4 GPa at 300/7 K. The pressure increases by $\sim 5\text{-}7$ GPa when the temperature is reduced from room temperature to 7 K. The green, blue and pink areas represent for the low- pressure regime, the medium pressure regime, and the high-pressure regime, respectively. The plots in (a)-(l) show an IMT appears at 22.0/29.6 GPa; The plots of (m)-(q) show that the superconducting transitions occur in Metal 2 at high pressure, and that the upper critical field of the superconducting transition is in between 6 and 7 T.

Figure 3. The results from Raman spectroscopy, XRD, and first-principles calculations. The green, blue and pink areas represent the low-pressure regime, the medium pressure regime, and the high-pressure regime, respectively. The Raman spectra were collected simultaneously with electrical resistance from 0.8 to 61.4 GPa and temperature at (a) 300 K and (b) 7 K. The overall intensity is significantly reduced due to metallization at 22.0 GPa, indicating a correlation between the IMT and structure changes. Below the IMT pressure, the Raman peak 2 continuously softens with compression prior to the IMT. Diffraction patterns displayed in (c) are collected at 300 K where a structure transition appears above 23.4 GPa. The new high-pressure phase continuously evolves

with pressure and eventually becomes stable above 39.9 GPa. The structure models resulted from the diffraction pattern refinement are shown in (d)–(f). (g) The calculated band structure of the Metal 2 phase. The violet and green lines represent the result with and without SOC, respectively. (h) The projected DOS for the Metal 2 phase around the Fermi level. Gray-, green-, blue-, and red-shaded regions represent the projected DOS onto the bonding orbitals of the molecular e , a_1 , $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 1/2$ states, respectively. It is clear that the molecular orbital nature is no longer well retained in this high-pressure regime. The black and magenta solid lines refer to the Ta- t_{2g} and the anti-bonding orbital state, respectively.

Figure 4. Pressure-temperature phase diagram of GaTa₄Se₈. The solid black lines represent the phase boundary as defined by transport measurements. The green, cyan, light-blue and yellow colors the insulating, bad metallic (or weakly insulating), Metal 1 and Metal 2 phase, respectively. Two distinctive superconducting (SC) phases are presented in the orange and pink color with a solid red line. The phase boundary for the first one (SC 1) is taken from Ref.¹¹. The different-colored circles represent the distinctive Raman modes (as shown in Figures 1 and 3). We note that very recently the tetragonal phase is reported at ambient pressure under 50 K by Ishikawa et al²¹.

Figure 1

Figure 2

Figure 3

Figure 4

METHODS

Sample preparation and characterization

Polycrystalline samples of GTS were prepared by the selenium transport method as described in Ref.¹³. The GTS powders were then placed in an evacuated silica tube with a small excess of Se and heated at 950 °C for 24 h and then slowly cooled (2 °C h⁻¹) to room temperature to avoid the selenium element vacancy. The sample was characterized by X-ray diffraction at HPCAT 16-BM-D, Advanced Photon Source, Argonne National Lab. Powder diffraction patterns were well indexed using the previously reported crystal structural data^{11,13,14}.

High-pressure X-ray powder diffraction

The pressure dependence of the lattice constants at room temperature up to about 8 GPa was measured on powder samples by angular dispersive X-ray diffraction (ADXRD) at HPCAT 16-BM-D using the symmetric diamond anvil cell (DAC) with Boehler-type diamonds and a T301 stainless steel gasket. Ne was loaded as the pressure transmitting medium to maintain good hydrostatic pressure. The incident X-ray beam size was ~10 µm with the energy 40 keV. The flow cryostat is applied to conductor the low temperature diffraction down to 30 K. A Mar345 CCD was used as the detector, and the on-line ruby system obtained the ruby fluorescence signal to determine the pressure. The imaged diffraction was integrated using the DIOPTAS software to acquire the diffraction intensity vs 2θ datasets. Crystallographic parameters and structure simulation were analyzed by Rietveld full-profile refinement using the General Structure Analysis System (GASA) program²⁴.

High-pressure Raman spectroscopy

Raman spectra were recorded in backscattering geometry using a micro-spectrometer with the symmetric cell. The DAC had a pair of 300 μm culet size ultralow fluorescence type II diamonds and was set in a microscopy cryostat system (Cryo Industries of America, Inc.) with a T301 steel gasket. The silicon diode sensor bought from Cryogenic Control Systems, Inc. was used for 30-300 K temperature calibration. A micro-Raman system (Renishaw, UK) with a 532 nm laser excitation was applied to obtain the sample's Raman spectra. A grating of 2400 grooves/mm was employed throughout the experiment, and the beam spot was about 20-30 μm . The ruby fluorescence was used to calibrate the pressure with a Ne as the pressure medium.

High-pressure X-ray absorption spectroscopy

The X-ray absorption spectroscopy (XAS) measurements were carried out in a transmission mode using the hard X-ray at beamline 20-ID-D of the Advanced Photon Source, Argonne National Laboratory. High pressure powder XAS was performed by a cross anvil cell with perforated nano-diamond to reduce the absorption from the diamond. The sample size of $\sim 30 \times 40$ (length and width) $\times 20$ (thickness) μm^3 was loaded into a sample chamber surrounded by a T301 steel gasket with small ruby chips as pressure calibrations. The sample chamber was sealed at ~ 1 GPa with silicon oil as the pressure medium. Measurements were collected at both the L_2 ($2p_{1/2} \rightarrow 5d$) and L_3 ($2p_{3/2} \rightarrow 5d$) absorption edges, which occur at energies of 11.136 keV and 9.880 keV with the elemental tantalum metal as the reference material. The acquired data was further analysis using the ATHENA software.

High-pressure electrical measurements

The electronic transport properties under high pressure and low temperature were investigated via four-probe electrical conductivity method in a CuBe alloy DAC. The pressure was generated by a

pair of diamonds with a 400 μm diameter culet. A gasket made of stainless steel was pressed, and a hole was drilled into the center of the gasket with a diameter of diamond culet. A cubic boron nitride (c-BN)-epoxy insulation layer was prepared to protect the electrode leads from the metallic gasket. Finally, a hole of 280 μm diameter was drilled in the center of the c-BN gasket. The NaCl powder was used as the pressure-transmitting medium. Four platinum strips were arranged to contact the sample in the chamber. The pressure-dependent resistance measurements were performed using a laboratory designed electrical transport system where a Keithley 6221 current source, 2182A nanovolt meter, and 7001 switch devices were used as the current supply, voltmeter, and voltage/current switcher, respectively. The experiments at different pressure-temperature conditions were performed using the Quantum Design Physical Properties Measurement System. The pressure was measured via the ruby fluorescence method at room temperature before and after cooling.

First-principles calculations

The electronic structure calculations based on density functional theory (DFT) were carried out by using ‘OpenMX’ code which is based on the linear combination of pseudoatomic orbitals²⁵. Local density approximation (LDA)^{26,27} was used for the exchange-correlation functional. Cutoff energy of 400 Ry and a $12 \times 12 \times 12$ Monkhorst-pack grid for momentum-space integration were adopted. The SOC was treated within the fully relativistic j -dependent pseudopotential and non-collinear scheme²⁸. The primitive unit cell of the experimentally determined $C2$ monoclinic structure was used for our calculations.

- 1 Yang, Z., Ko, C. & Ramanathan, S. Oxide electronics utilizing ultrafast metal-insulator transitions. *Annu. Rev. Mater. Res.* **41**, 337-367 (2011).
- 2 Aetukuri, N. B. et al. Control of the metal-insulator transition in vanadium dioxide by modifying orbital occupancy. *Nat. Phys.* **9**, 661-666 (2013).
- 3 Imada, M., Fujimori, A. & Tokura, Y. Metal-insulator transitions. *Rev. Mod. Phys.* **70**, 1039-1263 (1998).
- 4 Gray, A. X. et al. Correlation-driven insulator-metal transition in near-ideal vanadium dioxide films. *Phys. Rev. Lett.* **116**, 116403 (2016).
- 5 Wentzcovitch, R. M., Schulz, W. W. & Allen, P. B. VO₂: Peierls or Mott-Hubbard? A view from band theory. *Phys. Rev. Lett.* **72**, 3389-3392 (1994).
- 6 Cario, L., Vaju, C., Corraze, B., Guiot, V. & Janod, E. Electric-field-induced resistive switching in a family of Mott insulators: Towards a new class of RRAM memories. *Adv. Mater.* **22**, 5193-5197 (2010).
- 7 Guiot, V. et al. Avalanche breakdown in GaTa₄Se_{8-x}Te_x narrow-gap Mott insulators. *Nat. Commun.* **4**, 1722 (2013).
- 8 Inoue, I. H. & Rozenberg, M. J. Taming the Mott transition for a novel Mott transistor. *Adv. Funct. Mater.* **18**, 2289-2292 (2008).
- 9 Stoliar, P. et al. Universal electric-field-driven resistive transition in narrow-gap Mott insulators. *Adv. Mater.* **25**, 3222-3226 (2013).
- 10 Vaju, C. et al. Electric-pulse-driven electronic phase separation, insulator-metal transition, and possible superconductivity in a Mott insulator. *Adv. Mater.* **20**, 2760-2765 (2008).
- 11 Abd-Elmeguid, M. M. et al. Transition from Mott insulator to superconductor in GaNb₄Se₈ and GaTa₄Se₈ under high pressure. *Phys. Rev. Lett.* **93**, 126403 (2004).
- 12 Camjayi, A. et al. First-order insulator-to-metal transition in the paramagnetic 3D system GaTa₄Se₈. *Phys. Rev. Lett.* **113**, 086404 (2014).
- 13 Pocha, R., Johrendt, D., Ni, B. & Abd-Elmeguid, M. M. Crystal structures, electronic properties, and pressure-induced superconductivity of the tetrahedral cluster compounds GaNb₄S₈, GaNb₄Se₈, and GaTa₄Se₈. *J. Am. Chem. Soc.* **127**, 8732-8740 (2005).
- 14 Ta Phuoc, V. et al. Optical conductivity measurements of GaTa₄Se₈ under high pressure: evidence of a bandwidth-controlled insulator-to-metal Mott transition. *Phys. Rev. Lett.* **110**, 037401 (2013).
- 15 Wang, Y., Puggioni, D. & Rondinelli, J. M. Assessing exchange-correlation functional performance in the chalcogenide lacunar spinels GaM₄Q₈ (M = Mo, V, Nb, Ta; Q = S, Se). *Phys. Rev. B* **100**, 115149 (2019).
- 16 Reschke, S. et al. Lattice dynamics and electronic excitations in a wide series of lacunar spinels with breathing pyrochlore lattice structure. *Phys. Rev. B* **101**, 075118 (2020).
- 17 Jeong, M. Y. et al. Direct experimental observation of the molecular J_{eff} = 3/2 ground state in the lacunar spinel GaTa₄Se₈. *Nat. Commun.* **8**, 782 (2017).
- 18 Kim, H. S., Im, J., Han, M. J. & Jin, H. Spin-orbital entangled molecular jeff states in lacunar spinel compounds. *Nat. Commun.* **5**, 3988 (2014).
- 19 Jeong, M. Y. et al. M. J. Han Novel J_{eff} = 3/2 metallic phase and unconventional superconductivity in GaTa₄Se₈. (Submitted).

- 20 Park, M. J. et al. Pressure induced topological superconductivity in the spin-orbit Mott insulator GaTa₄Se₈. *npj Quantum Mater.* **5**, 41 (2020).
- 21 Ishikawa, H., Yajima, T., Matsuo, A., Ihara, Y. & Kindo, K. Nonmagnetic ground states and a possible quadrupolar phase in 4d and 5d lacunar spinel selenides GaM₄Se₈ (M = Nb, Ta). *Phys. Rev. Lett.* **124**, 227202 (2020).
- 22 Hlinka, J. et al. Lattice modes and the Jahn-Teller ferroelectric transition of GaV₄S₈. *Phys. Rev. B* **94**, (2016).
- 23 Rehr, J. J. & Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621 (2000).
- 24 Toby, B. H., & Von Dreele, R. B. "GSAS-II: the genesis of a modern open-source all purpose crystallography software package". *J. Appl. Crystallogr.* **46**, 544-549 (2013).
- 25 Ozaki, T. Variationally optimized atomic orbitals for large-scale electronic structures. *Phys. Rev. B* **67**, 155108 (2003).
- 26 Ceperley, D. M. & Alder, B. J. Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.* **45**, 566–569 (1980).
- 27 Perdew, J. P. & Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **23**, 5048 (1981).
- 28 MacDonald, A. H. & Vosko, S. H. Spin-polarized relativistic exchange energies and potentials. *J. Phys. C Solid State Phys.* **12**, 2977–2990 (1979).

Supplementary Information

Discovery of New Metallic and Superconducting Phase in GaTa₄Se₈ Under High Pressure

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1. The charge gap measured from resistance measurements

Figure S1. The results of electrical resistance follow an activation law $R(T) = \exp(\Delta/2k_B T)$ where Δ is the charge gap and k_B is the Boltzmann's constant. The value of Δ at each pressure point is obtained from linearly fitting the data to $\ln R(T)$ as a function of $1/T$. The charge gap becomes zero at 22.0/29.6 GPa, where an IMT occurs. Δ_0 is the charge gap at 0.8/5.0 GPa.

2. Pressure-dependent Raman data from a low to moderate pressure range

Figures 3(a, b) show the Raman spectra collected on the same sample during the electrical resistance measurements. The Raman peaks located in between 180 and 240 cm^{-1} are attributed to the vibrational mode of the Ta_4Se_4 (or Ta_4) cluster in the cubic GTS. Their splitting into two peaks (peak 1 and 2) starts to become obvious at around 1.8/7.5 GPa (at 300/7 K) and is enhanced. Peak 2 continuously softens at higher pressures prior to the IMT. At $P = 22.0/29.2$ GPa, a significant intensity reduction of the whole Raman spectra is noticed which is concomitant with an appearance of additional Raman peaks (peak 3 and 4). It signals a structural transition and this critical pressure

is consistent with that of IMT, $P_c \sim 22.0/29.6$ GPa, indicating a correlation between the structural transition and the IMT.

3. The crystal structure determined from XRD

	Cubic ($F\bar{4}3m$)	Monoclinic ($C2$)
	Ta ₄ Se ₄	Ta ₄ Se ₄
Symmetry	Td	C1
Average bond length (Å)	3.002	2.429
Distortion index (bond length)	0	0.0730
Distance between Clusters (Å)	4.322	3.908

Table S1. The structure solution and refinement indicate that the new phase above 23.4 GPa has a monoclinic $C2$ symmetry. The new monoclinic phase inherits the similar Ta₄Se₄ clusters to be basic units and the topological configurations of the cubic phase. Their difference lies in that (1) the distance between inter-clusters Ta₄Se₄ is reduced by 9.6% from 4.322 to 3.908 Å; (2) the symmetry of clusters Ta₄Se₄ and Ta₄ is reduced from Td to C1, and their distortion index (bond length) is 7.3% and 4.5%, respectively; (3) in the monoclinic phase, the averaged bond length of Ta—Se in Ta₄Se₄ is significantly reduced whereas the bond length of Ta—Ta in Ta₄ slightly increased. The distortion of the clusters and the shortening of inter-cluster distance should account for the metallization of the GTS and the drastic suppression of the Raman signal between 180-240 cm⁻¹. Such a structural transition is missed in previous studies.

4. Further discussion on superconductivity

Importantly, the superconductivity revealed in our experiments is distinct from the one reported by Abd-Elmeguid et al.: (1) The superconductivity observed in our experiments is ~20 GPa higher than that reported by Abd-Elmeguid et al.¹¹; (2) the metallic phase in our experiments

has lower symmetry than that of the insulating phase, whereas there is no structural transition is reported by Abd-Elmeguid et al.¹¹; (3) Abd-Elmeguid et al.¹¹ reported the T_c increases with pressure from 5.8 K at 12 GPa to ~ 8 K at 22 GPa, whereas we discovered that the T_c decreases slightly from 5.6 K at 32.0/41.1 GPa to 5.2 K at 60.7/68.2 GPa.

5. Superconductivity in Metal 1 regime

The previously reported superconductivity in the lower pressure range is not observed in our experiment. Although the reason for this is not entirely clear at this moment, we presume that it is likely attributed to the temperature limit in our experiment. As we mentioned in the main manuscript, our experimental set-up carefully takes into account of pressure change caused by temperature change and vice versa. In fact, we found that T_c varies with the current or voltage applied in the resistance measurements, which possibly causes the inconsistency. We failed to lower the temperature below ~ 5 K in the pressure regime of Metal 1, which is likely the main reason why the superconductivity of Metal 1 (the one previously reported) is not clearly observed in our experiment.

6. Characteristics of Metal 2 phase

In order to unveil the detailed characteristics of Metal 2 phase, we performed the theoretical analysis. The DFT calculations show that the projected DOS onto atomic Ta- t_{2g} orbitals is distributed over the energy range of ~ 15 eV at 50.2 GPa with our OpenMX-PAO (pseudo-atomic orbital) basis projection although defining the local axis for t_{2g} states are not well defined due to the significant distortion of Ta₄Se₄ cluster. By projecting the whole d orbital complex, we obtained the bandwidth is $W \sim 20$ eV. The use of another projector based natural atomic orbital (NAO)²⁹, the estimated bandwidth is similar $W \sim 20$ eV; see Figure S2. Using maximally localized Wannier function, we failed to reproduce the DFT band structure for Ta- t_{2g} states likely due to the strong p - d hybridization at this high pressure.

The on-site Coulomb interaction, Hubbard U , and the SOC strength λ for Ta-5d electrons is about 2-3 eV and 0.2-0.5 eV, respectively³⁰. Considering the bandwidth W in this Metal 2 pressure regime, U/W and λ/W is therefore ~ 0.1 -0.2 and ~ 0.01 -0.03, respectively. With this set of parameters, Fermi liquid behavior for Metal 2 is expected. According to the previous Hubbard model DMFT studies^{31,32}, it is clearly in the Fermi liquid regime for the case of $\lambda = 0$. For $\lambda/W = 0.125$ ³² (which is still order-of-magnitude larger), it goes closer to non-Fermi liquid area, but remains as Fermi liquid phase. Thus, our theoretical analysis shows that the newly-discovered Metal 2 phase is most likely Fermi liquid.

Experimental data, on the other hand, do not show a clear Fermi liquid behavior as shown our transport data in Figure 2. We presume that it is attributed to the extrinsic effect such as grain boundary effect and impurity which was also observed in the other transport measurement of this material¹¹.

Figure S2. The projected DOS of Ta- d orbitals with NAO projector. The black, green, red and blue line represents the projected DOS for each Ta atom in the Ta₄Se₄ cluster.

- 30 Şaşioğlu, E., Friedrich, C. & Blügel, S. Effective Coulomb interaction in transition metals from constrained random-phase approximation. *Phys. Rev. B* **83**, 121101 (2011).
- 31 Werner, P., Gull, E., Troyer, M. & Millis, A. J. Spin freezing transition and non-Fermi-liquid self-energy in a three-orbital model. *Phys. Rev. Lett.* **101**, 166405 (2008).
- 32 Kim, A. J., Jeschke, H. O., Werner, P. & Valentí, R. J. Freezing and Hund's rules in spin-orbit-coupled multiorbital Hubbard models. *Phys. Rev. Lett.* **118**, 086401 (2017).

Figures

Figure 1

The XRD, Raman spectroscopy, and EXAFS measurements on GTS in low-high pressure regime. The pressure values (unit: GPa) are printed close to each pattern. (a) XRD patterns were obtained from 0.8 to 8.0 GPa at 30 K, and no structural change is observed; (b) Raman spectra were collected from 0.4 to 10 GPa at room temperature. The peak 1 between 200 and 250 cm^{-1} that splits into two peaks appears at 4.2 GPa; (c) The EXFAS spectra are measured from 0.7 to 5.4 GPa at room temperature and significant broadening of the second peak 2 occurs above 1.9 GPa. The insets are the model of the Ta₄Se₄ clusters.

Figure 2

The plots of electrical resistance measurements ranging from 0.8/5.0 GPa to 61.4/68.4 GPa at 300/7 K. The pressure increases by ~ 5 -7 GPa when the temperature is reduced from room temperature to 7 K. The green, blue and pink areas represent for the low- pressure regime, the medium pressure regime, and the high-pressure regime, respectively. The plots in (a)-(l) show an IMT appears at 22.0/29.6 GPa; The plots of (m)-(q) show that the superconducting transitions occur in Metal 2 at high pressure, and that the upper critical field of the superconducting transition is in between 6 and 7 T.

Figure 3

The results from Raman spectroscopy, XRD, and first-principles calculations. The green, blue and pink areas represent the low-pressure regime, the medium pressure regime, and the highpressure regime, respectively. The Raman spectra were collected simultaneously with electrical resistance from 0.8 to 61.4 GPa and temperature at (a) 300 K and (b) 7 K. The overall intensity is significantly reduced due to metallization at 22.0 GPa, indicating a correlation between the IMT and structure changes. Below the IMT pressure, the Raman peak 2 continuously softens with compression prior to the IMT. Diffraction patterns displayed in (c) are collected at 300 K where a structure transition appears above 23.4 GPa. The new high-pressure phase continuously evolves with pressure and eventually becomes stable above 39.9 GPa. The structure models resulted from the diffraction pattern refinement are shown in (d)–(f). (g) The calculated band structure of the Metal 2 phase. The violet and green lines represent the result with and without SOC, respectively. (h) The projected DOS for the Metal 2 phase around the Fermi level. Gray-, green-, blue-, and redshaded regions represent the projected DOS onto the bonding orbitals of the

molecular e, a_1 , $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 1/2$ states, respectively. It is clear that the molecular orbital nature is no longer well retained in this high-pressure regime. The black and magenta solid lines refer to the Ta- t_{2g} and the anti-bonding orbital state, respectively.

Figure 4

Pressure-temperature phase diagram of GaTa₄Se₈. The solid black lines represent the phase boundary as defined by transport measurements. The green, cyan, light-blue and yellow colors the insulating, bad metallic (or weakly insulating), Metal 1 and Metal 2 phase, respectively. Two distinctive superconducting (SC) phases are presented in the orange and pink color with a solid red line. The phase boundary for the first one (SC 1) is taken from Ref.11. The different-colored circles represent the distinctive Raman modes (as shown in Figures 1 and 3). We note that very recently the tetragonal phase is reported at ambient pressure under 50 K by Ishikawa et al²¹.

Supplementary Files

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