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Band gap crossover and insulator–metal transition in the compressed layered CrPS₄

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Two-dimensional van der Waals (vdW) magnetic materials have emerged as possible candidates for future ultrathin spintronic devices, and finding a way to tune their physical properties is desirable for wider applications. Owing to the sensitivity and tunability of the physical properties to the variation of interatomic separations, this class of materials is attractive to explore under pressure. Here, we present the observation of direct to indirect band gap crossover and an insulator–metal transition in the vdW antiferromagnetic insulator CrPS₄ under pressure through in-situ photoluminescence, optical absorption, and resistivity measurements. Raman spectroscopy experiments revealed no changes in the spectral feature during the band gap crossover whereas the insulator–metal transition is possibly driven by the formation of the high-pressure crystal structure. Theoretical calculations suggest that the band gap crossover is driven by the shrinkage and rearrangement of the CrS₆ octahedra under pressure. Such high tunability under pressure demonstrates an interesting interplay between structural, optical and magnetic degrees of freedom in CrPS₄, and provides further opportunity for the development of devices based on tunable properties of 2D vdW magnetic materials.

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INTRODUCTION

Ever since the successful exfoliation of stable single-layer graphene¹, research on layered two-dimensional van der Waals (2D vdW) materials has attracted significant interests in the past decade. One of the current focuses is the investigation of magnetic 2D vdW materials, which is quite attractive from both a fundamental physics and practical application perspective (e.g., refs 2–4). In principle, the discovery of atomically thin materials with intrinsic ferromagnetism and high-magnetic ordering temperature could open up opportunities to realize spintronic devices, such as molecular quantum devices and high-density ultrathin storage devices. Indeed, the recent groundbreaking experimental observations of the intrinsic magnetism in atomically thin FePS₃, CrI₃, Cr₂Ge₂Te₆, and Fe₃GeTe₂^{5–11} have pushed this class of materials to be promising candidates for possible applications in spintronic technology, as they can serve as building blocks for magnetic vdW heterostructures.

In order to explore the wider applications of 2D vdW materials, it is necessary to tune their optical, electronic, and magnetic properties. Several attempts have been made to tune the properties of 2D vdW magnets, such as by intercalation, gating, electrostatic doping, and changing layer thickness to name a few (e.g., refs 9,12–17). Pressure or compressive strain might also be an alternative way to tune the properties of the 2D vdW magnets without introducing disorder or impurities to the system. It has been recently shown that pressure can be effectively used to modify the magnetic, electronic, and optical properties of 2D vdW magnets both in bulk and atomically thin samples^{18–29}.

Among the 2D vdW magnetic materials, CrPS₄ is currently enjoying a surge of interest^{30–35}. CrPS₄ was first synthesized in the 1970s and found to possess a monoclinic symmetry (C2/m space group)³⁶. In the structure, puckered layers of S atoms are arranged

in hexagonal close packing parallel to the a-axis, whereas the Cr atoms form a square lattice. Each Cr atom is surrounded by six S atoms forming a slightly distorted octahedron, and three CrS₆ octahedra are connected by a single P atom (Fig. 1(a)). It is an antiferromagnetic semiconductor with a band gap of ~1.4 eV^{30,37}. Previous magnetic studies suggested a C-type antiferromagnetic structure (antiferromagnetic interaction within a layer and ferromagnetic interaction between the layer) below the Néel temperature (T_N) of 36 K³⁸. However, recent neutron diffraction and torque magnetometry investigations revealed an A-type AFM structure with the intralayer ferromagnetic interaction and interlayer antiferromagnetic coupling along the c axis³⁵. X-ray spectroscopy studies demonstrated that the Cr 3d bands are localized within the energy gap in the vicinity of the Fermi level, where the lower and higher energy of the band structure is dominated by the non-bonding S 3p band and the S 3s band, respectively³⁹. Theoretical calculations predicted that CrPS₄ is stable in the monolayer form while retaining the intrinsic magnetism and semiconducting properties⁴⁰. Lee et al.³⁰ reported thickness-dependence studies of the structural, vibrational, and optical properties of CrPS₄ where they observed the disappearance of Raman peaks and weakening of the photoluminescence signal in the monolayer limit due to photodegradation of the thin sample³⁰. Symmetry breaking was found to induce the appearance of Fano resonance in the photoluminescence spectra of CrPS₄ collected below the antiferromagnetic transition³⁴.

With its rich optical and electronic properties, exploring the tunability of CrPS₄ by the application of pressure is beneficial, not only to improve the clear understanding of the physical properties but also to investigate the wider potential applications of this material. However, the high-pressure behavior of CrPS₄ remains unexplored to date. By comparison, high-pressure investigations

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Fig. 1 Crystal structure and optical characterization of CrPS₄. **a** Crystal structure of CrPS₄ with the *C2/m* space group. **b** Room temperature photoluminescence and optical absorption spectra of CrPS₄ below 1 GPa. Inset shows the deconvoluted PL spectrum fitted with two Voigtian peaks. **c** Molecular orbital energy diagram involved in the optical transitions of CrPS₄. The blue and red arrows indicate *d–d* transitions and the orange arrow represents a possible ligand-to-metal charge-transfer (LMCT) transition. **d** Configurational diagram of Cr³⁺ for the observed absorption (blue arrows) and PL (red arrows) spectra.

on the closely related systems such as TMP(S, Se)₃ (TM = transition metal) in which the TM ions form a layered honeycomb lattice, have revealed Mott insulator–metal and structural transitions in MnPS₃¹⁸, FePS₃^{20,25,27}, FePSe₃²⁵, and recently Mott isostructural transition in V_{0.9}PS₃²⁶.

In this work, we examine the effects of pressure on the optical, electronic, and vibrational properties of layered CrPS₄ through the use of optical absorption, photoluminescence, resistivity, and Raman spectroscopy measurements. We observed anomalous changes in the photoluminescence and optical absorption spectra on compression above ~3 GPa. Further compression leads to an insulator–metal transition, which begins above 15 GPa as evidenced by the optical absorption and resistivity data. Raman spectroscopy measurements indicates that the crystal structure is

stable below 10 GPa. However, the Raman spectra significantly changes above 16 GPa, which suggests the formation of a high-pressure phase accompanying the insulator–metal transition in CrPS₄. Theoretical calculations show that the anomalies observed in the photoluminescence and optical absorption data above 3 GPa are related to the direct to indirect band gap crossover, which is mainly driven by the rearrangement of the CrS₆ octahedra under pressure.

RESULTS AND DISCUSSION

Optical properties under pressure

The photoluminescence (PL) and optical absorption spectra of CrPS₄ at the lowest pressure of our measurements (*P* < 1 GPa) are

Fig. 2 High-pressure photoluminescence properties of CrPS₄. **a** Room temperature PL spectra of CrPS₄ as a function of pressure. The spectra are shifted for clarity. The derived pressure dependences of **(b)** PL peak position and **(c)** intensity of the PL peak integrated from 1.2 to 1.5 eV.

presented in Fig. 1(b). Both spectra are similar to those reported previously at ambient pressure, which suggests that the optical and electronic properties of the sample are not affected by the application of pressure <1 GPa. As shown in Fig. 1(b), the sample at 0.9 GPa exhibits a broad PL peak centered at ~1.3 eV, in agreement with the PL spectrum at ambient conditions^{30,34}. The PL spectrum consists of two Voigtian components centered at ~1.3 and ~1.37 eV, respectively (A and B components in the inset of Fig. 1(b)). Previous studies showed that the intensity of the PL peak of CrPS₄ increases linearly with increasing laser power without any signs of saturation, ruling out the possible excitonic emission of the PL in CrPS₄³⁴. In CrPS₄ crystal, the Cr³⁺ ion is located in a distorted octahedral environment formed by six S atoms. In this case, the octahedral crystal field will split the 3d orbital of Cr³⁺ into t_{2g} and e_g orbitals with a splitting energy of $\Delta \sim 2.0$ eV³⁹ (Fig. 1(c)), and the electronic configuration of Cr³⁺ (d^3 configuration, 4F term) splits into the $^4A_{2g}$ ground state and $^4T_{2g}$ and $^4T_{1g}$ excited states (Fig. 1(d)). The PL peak observed in CrPS₄ has been previously attributed to the spin-allowed $d-d$ transition of the Cr³⁺ ion^{30,34} (red arrows in Fig. 1(c, d)), which are often located around 1.6–2.2 eV in the Cr-based compounds^{41,42}.

The optical absorption spectrum exhibits three clear features (marked by T_1 , T_2 , and T_3). The feature at T_3 has been assigned to the ligand-to-metal charge-transfer (LMCT) transition from the 3p of the S band to the unoccupied 3d band of the Cr atom^{30,39} (orange arrow in Fig. 1(c)). In the lower energy region, two weaker (T_1 and T_2) peaks located at ~1.6 and ~1.8 eV can be observed. These two absorption peaks can be assigned to the spin-allowed $d-d$ transitions (blue arrows in Fig. 1(c, d))^{30,34}, which are forbidden according to the Laporte parity selection rule. Despite being forbidden, these $d-d$ transitions can be weakly allowed due to local symmetry breaking⁴³. A large Stokes shift between the PL peak and the T_1 peak in the absorption spectra of ~300 meV is due to the Franck-Condon principle and strong electron-lattice coupling⁴⁴. Both PL and absorption data, therefore, indicate that CrPS₄ possesses a band gap of ~1.3 eV, which is governed by the Cr $d-d$ transition.

In order to investigate the evolution of electronic structures under pressure, we measured in-situ PL and optical absorption

data. Figure 2(a) shows the PL spectra of single crystal CrPS₄ at room temperature collected up to 11.8 GPa. Under compression to 1.8 GPa, the PL A peak slightly blue-shifts to higher energy whereas the position of the B peak remains constant (Fig. 2(b) and Supplementary Fig. 3). Above 2 GPa the A peak gradually moves to lower energy and the B peak disappears while a new PL peak simultaneously appears at lower energy (marked by C in Fig. 2(a) and Supplementary Fig. 3). The A peak is no longer observable above 8 GPa while the C peak remains up to 10 GPa, above which the entire PL signal of CrPS₄ disappears.

The pressure dependence of the PL peak intensity (integrated from 1.2 to 1.5 eV) is shown in Fig. 2(c). The PL peak intensity of CrPS₄ continuously decreases with increasing pressure and the PL signal completely disappears above 10 GPa. A clear change in slope is observed at around 2.5 GPa, similar to the pressure where the new PL (C) peak starts to emerge. One possible explanation for the observed change in the PL spectra and intensities of CrPS₄ under pressure might be the band gap crossover (direct to indirect band gap). Similar behavior in the PL spectra has been observed previously in several systems such as InP⁴⁵, InSe⁴⁶ and monolayer MoS₂⁴⁷, and has been attributed to the direct-indirect gap crossover induced by pressure. However, given that the PL signal of CrPS₄ arises from the parity forbidden $d-d$ transition, which is sensitive to the CrS₆ octahedra, the anomalous behavior of PL data above 3 GPa could be related to a subtle change in the crystal structure, possibly a modification of the CrS₆ octahedra under pressure.

In Fig. 3(a), we present the Tauc plot $((\hbar\nu)^2$ versus the photon energy $\hbar\nu$) of the low-energy region of the room temperature optical absorption data measured up to 27 GPa. Given that the strong absorption edge at ~2 eV is related to the LMCT transition, we focus our analyses on the evolution of band gap associated with the $d-d$ (T_1 and T_2) transitions as described in Fig. 1 and Supplementary Fig. 4. The derived band gaps are shown in Fig. 3(b). The band gaps for the T_1 and T_2 transitions at 0.8 GPa are ~1.5 and ~1.6 eV, respectively. These band gaps are relatively unchanged as the pressure is increased to ~4 GPa. Interestingly, the T_1 peak and its associated band edge disappears above 4 GPa, whereas the T_2 peak remains (see Supplementary Fig. 5). The band gap for the T_2 transition slightly increases above 5 GPa before it

Fig. 3 High-pressure evolution of optical absorption of CrPS_4 . **a** Tauc plot $((ah\nu)^2$ versus the photon energy $h\nu$) of room temperature optical absorption spectra of CrPS_4 at various pressures. The spectra are shifted for clarity. **b** The derived optical band gaps associated with the Cr $d-d$ (T_1 and T_2) transitions in CrPS_4 at high pressures.

Fig. 4 Electrical transport properties of CrPS_4 under pressure. **a** Pressure-dependence resistivity of CrPS_4 at room temperature. **b** Temperature-dependence resistivity of CrPS_4 obtained at various pressures. Inset shows the temperature-dependence resistivity at 6.7 GPa measured from room temperature to 420 K.

starts to decrease above 12 GPa. A clear absorption edge is no longer observable above 19 GPa, which suggests a pressure-induced metallization in CrPS_4 above 18 GPa. The overall behavior of the band gap derived from the absorption data (Fig. 3(b)) is similar to that of the PL data. In particular the band gap of CrPS_4 , governed by the Cr $d-d$ transition, seems to undergo an anomalous change above 4 GPa. The band gap slightly increases on further compression to ~ 12 GPa, above which it begins to narrow and finally closes above 19 GPa.

Electronic transport properties

The effects of pressure to the electronic properties and possible pressure-induced metallization of CrPS_4 is further investigated by electrical transport measurements. In Fig. 4(a) we present the pressure dependence of resistivity of CrPS_4 measured at ambient because the resistivity value of CrPS_4 below 5 GPa was beyond the sensitivity of the equipment used. The resistivity values between 5 and 10 GPa are in the order of $\sim 10^5 \Omega \text{ cm}$, which indicates an extremely insulating sample. However, on increasing pressure, the

Fig. 5 High-pressure Raman spectroscopy measurements. **a** Selected Raman spectra of CrPS₄ at various pressures. Asterisks mark the strongest Raman modes in the HP phase of CrPS₄. The dot represents an unknown Raman mode. **b** Pressure dependence of Raman shifts.

resistivity rapidly drops from $\sim 10^5 \Omega \text{ cm}$ at 10 GPa to a less than $\sim 10^{-1} \Omega \text{ cm}$ above ~ 15 GPa. Such a huge drop in resistivity indicates that CrPS₄ undergoes a pressure-induced insulator–metal transition above ~ 15 GPa, which is further confirmed by the temperature-dependent data shown in Fig. 4 (b). The insulating behavior is recovered upon releasing pressure, which indicates a reversible insulator–metal transition in CrPS₄. The corresponding conductivity data (Supplementary Fig. 6) follows a scaling behavior of $(\sigma - \sigma_c) \sim (P - P_c)^\gamma$ with a critical exponent of $\gamma = 3$ and the critical pressure P_c of 13(1) GPa. Similar scaling behavior has been observed in the conductivity of Cr-doped V₂O₃⁴⁸ and PbCrO₃⁴⁹.

The temperature-dependent data below 10 GPa measured from room temperature to 420 K (inset of Fig. 4(b)) reveals that the resistivity decreases as the temperature is increased, thus, confirming the insulating behavior of CrPS₄ at low pressures. Similarly, resistivity data at 13.6 GPa measured down to 50 K also shows that the sample possesses semiconducting behavior where the resistivity increases as the temperature is lowered. Further compression leads to the suppression of the semiconducting behavior, and the temperature-dependence data collected above 19 GPa shows a positive slope confirming the fully metallic state of CrPS₄ at high pressures, consistent with the optical absorption data. No drop in resistance nor zero resistance at low temperature was observed in the metallic state of CrPS₄ thus ruling out the emergence of pressure-induced superconductivity, such as those observed in other van der Waals magnetic insulators such as FePSe₃²⁵ and CrSiTe₃²⁹.

High-pressure Raman spectroscopy

High-pressure Raman spectroscopy measurements were then performed to provide insights into the vibrational properties of CrPS₄ under pressure. Figure 5(a) shows Raman spectra of CrPS₄ measured at various pressures from 1.2 up to 32 GPa. The Raman spectrum taken at the lowest pressure of 1.2 GPa consists of 13 active Raman modes, consistent with the Raman spectrum at ambient conditions^{30,34}. Upon compression to 10 GPa (region I), most of the Raman modes shift towards higher frequencies (hardens) except the M2 mode at around 170 cm⁻¹, which softens with increasing pressure (Fig. 5(b) and Supplementary Fig. 7). Interestingly, the relative intensity between the M6 and M7 modes (I_6/I_7) anomalously increases above 5 GPa, whereas the M2 and M3

Raman modes seem to undergo a crossover above 4 GPa (Supplementary Fig. 7). Despite these changes, no significant differences were observed in the Raman spectra up to ~ 14 GPa.

Between 15 and 20 GPa (region II), we observed the disappearance of several Raman modes observed in region I, as well as the emergence of new Raman modes. The intensities of all Raman peaks are weakened above 15 GPa due to the fact that the sample approaches its fully metallic state. Above 20 GPa (region III), where optical absorption and resistivity data show a metallic behavior, the Raman spectra consist of three Raman modes corresponding to the high-pressure phase of CrPS₄. Further compression does not lead to the appearance of new Raman modes and no changes in the Raman spectra are observed up to 30.4 GPa. Similar to the electrical transport data, the Raman spectrum returns to its original feature upon decompression to ambient pressure.

Electronic structures of CrPS₄ at high pressure

To understand the change in electronic structures observed experimentally, we performed density functional theory (DFT) and DFT + dynamical mean field theory (DMFT) calculations. Owing to the lack of a detailed crystal structure under pressure, we first optimized the structure using the DFT + U method. We note that the additional phonon and Raman calculations we conducted at 0 and 10 GPa to verify the predicted crystal structure under pressure revealed no dynamical instabilities both at 0 and 10 GPa (Supplementary Fig. 8). The calculated Raman spectra are also similar to those measured experimentally (see Supplementary Fig. 8), indicating that our analysis based on the optimized structure from the ab initio calculation (shown below) is reasonable despite the absence of X-ray diffraction data.

Based on the optimized structure from the DFT + U calculations, we performed a paramagnetic (PM) DFT + DMFT calculation because the optical properties under pressure were collected at room temperature (much higher than $T_N \sim 38$ K). The calculated band structure at $T \sim 298$ K are presented in Fig. 6. Owing to the strong electron correlation effect, half-filled Cr t_{2g} orbitals split into lower Hubbard bands and upper Hubbard band, making a Mott gap (Supplementary Fig. 9). Cr e_g bands are located around 2.5 eV while the occupied S p bands dominate the valence band (VB) below -1 eV. CrPS₄ at ambient pressure shows a direct-band gap at the Γ point. The band gap is estimated to be around 1.5 eV, which is governed by the Hubbard bands of Cr t_{2g} orbitals. Owing

Fig. 6 Theoretical calculations on CrPS₄. **a** Band structures of CrPS₄ at 298 K calculated at various pressures. The k -points Γ , X, A, Y, Z represent the (0, 0, 0), (0.5, 0, 0), (0.5, 0.5, 0), (0, 0.5, 0), and (0, 0, 0.5) points in the conventional Brillouin zone. **b** The CrS₆ octahedra environment in CrPS₄ and **c** pressure dependence of the calculated Cr–S bond lengths.

to the nearly flat conduction band (CB) along the $\Gamma - Z$ direction, an indirect transition between VB at Γ point and CB at Z point cannot be ruled out. The calculated energy gap is consistent with the observation of the PL signal centered at around 1.3 eV.

One of the main changes in electronic structure under pressure is the band dispersion in CB along the $\Gamma - Z$ direction. The Z point energy of CB is downshifted compared with the Γ point due to the decrease in the interlayer distance as pressure increases. At 2 GPa, this shift of the CB slightly changes the nature of the band gap, from a direct to indirect gap between VB at the Γ point and CB at the Z point. Above 2 GPa, another noticeable change is observed where the second highest VB moves upward (see the Γ point). As a result, the VB maximum shifts from Γ to between Γ and Y points at 6 GPa so that the momentum mismatch of the indirect transition increases. This indicates that the anomalous behaviors of the PL and absorption data of CrPS₄ above 3 GPa is related to the direct to indirect band gap crossover (Fig. 2).

To understand the origin of the direct-indirect crossover, we investigated the pressure dependence of the bond length of the Cr–S bonds based on the optimized crystal structure obtained from the DFT + U calculations. Owing to the crystal symmetry, there are three types of Cr–S bonds in the CrS₆ octahedra as shown in Fig. 6(b). The calculated Cr–S bond lengths at ambient pressure are well matched with the available experimental results, where the Cr–S3 bond is the longest in the octahedra. Upon compression, the Cr–S3 bond length decreases much faster than the Cr–S2 bond length resulting in a bond length crossover where the Cr–S2 bond becomes the longest above 5 GPa (Fig. 6(c)). This bond length crossover agrees well with the VB maximum crossover discussed above. As the bond length difference between Cr–S2 and Cr–S3 decreases, the second highest VB originating from the Cr t_{2g} band moves upward (Supplementary

Fig. 9). Above 5 GPa where the Cr–S2 bond becomes longer than the Cr–S3 bond, the VB maximum shifts from Γ to between the Γ and Y point. This implies that the band gap crossover is driven by the shrinkage and rearrangement of the CrS₆ octahedra. We note that the agreement between the Cr–S bond length crossover from our calculations and the M2 and M3 modes crossover observed in the experimental and calculated Raman spectra above 4 GPa (Supplementary Figs. 7 and 9) suggests that the M2 and M3 modes might be related to the vibration of the Cr–S bonds in the CrS₆ octahedra.

Having found the occurrence of band gap crossover in CrPS₄, we then investigated the possible magnetic transformation under pressure as derived from the DFT + U ($U = 2$ eV) calculations. At ambient pressure, we found that the A-type AFM structure is the most energetically favorable state, consistent with previous DFT studies⁴⁰ and recent neutron diffraction experiments³⁵. Our calculations suggest that the A-type AFM structure remains stable and no signs of change in the magnetic state is predicted to occur under pressure up to 20 GPa (see Supplementary Fig. 10). This suggests that the magnetism of CrPS₄ is not affected by the band gap crossover. However, further studies using susceptibility measurements under high pressure will clearly be beneficial to investigate the evolution of magnetism of CrPS₄ experimentally.

Finally, the nature of the pressure-induced insulator–metal transition in CrPS₄ is addressed. As shown above, the Raman spectroscopy experiments suggest a possible structural transition accompanying the insulator–metal transition that occurs above 15 GPa. However, whether the structural transformation is an isostructural transition or rather involves the formation of a high-pressure phase remains unclear. Based on the optimized structure from DFT + U calculations and assuming that the monoclinic $C2/m$

space group is stable at high pressure, our DFT + DMFT calculation at 20 GPa shows that CrPS₄ remains an insulator with a band gap of 0.7 eV. We also calculated the electronic structure at 20 GPa using smaller interaction parameters ($U = 8$ eV, $J = 0.8$ eV). However, the system is still a Mott insulator with a band gap of 0.4 eV. Our DFT + DMFT calculations indicate that the metallization based on the $C/2m$ structure occurs at much higher pressure ($P > 30$ GPa) than that observed in the experiment. This implies that the insulator–metal transition in CrPS₄ could be accompanied by the formation of a new high-pressure phase as inferred from the Raman spectroscopy data. While the pressure dependence of conductivity follows a mean field exponent (an indication of a Mott transition), it appears that the mechanism behind the insulator–metal transition in CrPS₄ cannot be solely attributed to the bandwidth-controlled Mott transition and the formation of high-pressure phase might play an important role in the metallization process. More X-ray diffraction experiments will be carried out in the near future to determine the nature of the structural transition above 15 GPa.

The observation of a direct to indirect band gap crossover and insulator–metal transition in the layered antiferromagnetic insulator CrPS₄ under pressure has been demonstrated. While the band gap crossover above 3 GPa is due to the shrinkage and rearrangement of the CrS₆ octahedra without a change in the crystal symmetry, it appears that the insulator–metal transition could be accompanied by a structural phase transition above 15 GPa. These highly tunable properties highlight the strong interplay between the structural, optical, electronic and magnetic properties in CrPS₄ and show great potential for device applications based on van der Waals materials.

METHODS

Sample preparation and characterizations

A single crystal of CrPS₄ was prepared by the chemical vapor transport method. The stoichiometry ratio of Cr, P, and S powders were mixed and put into a sealed quartz tube. The sealed tube was then put into a two-zone tube furnace and heated up for 24 h. The hot side was 730 °C while the cold side was about 680 °C, and was maintained for 7 days, then slowly cooled down to room temperature with 100 °C h^{−1}. X-ray diffraction patterns of the single crystal and pulverized samples were collected using the Rigaku Miniflex diffractometer (Cu-Kα radiation) (Supplementary Notes). The magnetic properties were measured by the Quantum Design magnetic property measurement system (MPMS-XL5) (Supplementary Notes).

High-pressure experiments

The resistivity data at high pressure were collected in two runs. In the first run, we measured the high-pressure resistivity data with a symmetric diamond anvil cell (DAC) at ambient temperature using a Keithley 6221 current source, 2182A nanovoltmeter, and a 7001 switch system as the current source, voltmeter, and voltage/current switcher, respectively. In the second run, we measured the resistivity of CrPS₄ from 300 to 2 K up to ~31 GPa in a homemade multifunctional measurement system (1.6–300 K; 0–9 T, Cryomagnetics Inc.) using a DAC made of a Be–Cu alloy. The size of the diamond culet used was 300 μm in diameter for all runs. A mixture of epoxy and Cubic boron nitride (cBN) powder was used as a sample chamber and acted as an insulating layer between the electrodes and the stainless steel gasket. The CrPS₄ single crystal was cut into a square of approximately 60 μm in width and 10 μm in thickness. Soft hBN powder was used as a pressure medium. We used the van der Pauw four probe method to measure the electrical resistance using platinum (Pt) foil as electrodes. Several ruby balls were loaded into the sample chamber as pressure calibrants⁵⁰.

The photoluminescence (PL) and Raman measurements were performed in a DAC at room temperature. A small piece of single crystal together with several ruby balls, were placed in a stainless steel gasket with a hole of 120 μm diameter. For the measurement of the Raman and PL emission spectra, a Renishaw in Via Raman system with a laser of 532 nm wavelength was used as an excitation source. High-pressure ultra-visible

absorption measurements were performed by a UV–Vis Absorption and Transmission Spectrometer System in a DAC with type-II diamonds up to 25 GPa. A mixture of methanol–ethanol (4:1 volume ratio) or silicone oil was used as a pressure transmitting medium.

Theoretical calculations

To study the correlated electronic structure of CrPS₄, we employed the embedded DMFT combined with DFT (DFT + DMFT) as implemented in the WIEN2k + eDMFT package⁵¹. The WIEN2k calculations were performed using the PBE-GGA functional⁵² with 1000 *k*-points. The correlation effect of Cr 3*d* orbitals was treated by a DMFT loop on the top of an effective one-electron Hamiltonian generated from the WIEN2k calculation. A hybridization energy window from −10 to 10 eV with respect to the Fermi level was chosen, and the Coulomb interaction of $U = 10$ eV and Hund's coupling of $J = 1$ eV were used for the Cr *d* orbitals. The local impurity problem was solved by using continuous time quantum Monte Carlo (CTQMC)⁵³. For the structural optimization at different pressure, we used the Vienna ab initio package (VASP)⁵⁴, where the plane-wave cut off was set to 500 eV. The DFT-D3 functional was used to describe the van der Waals (vdW) interaction⁵⁵.

DATA AVAILABILITY

All relevant data are available from the authors upon reasonable request.

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AUTHOR CONTRIBUTIONS

R.A.S., B.G.Y., and B.C. designed and conceived the project. Q.D. and C.P. synthesized the sample and carried out basic characterizations. R.A.S., J.J.F., and H.L.D. carried out resistivity measurements. Z.Y. performed the UV–Vis optical absorption experiments. R.A.S. and M.Z.Y. performed photoluminescence and Raman spectroscopy experiments. B.G.J., J.H.S., and D.Y.K. performed theoretical calculations. R.A.S., B.G.J., and J.J.F. analyzed the data and wrote the paper with the contributions from other co-authors.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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