Superatomic Two-Dimensional Semiconductor

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ABSTRACT: Structural complexity is of fundamental interest in materials science because it often results in unique physical properties and functions. Founded on this idea, the field of solid state chemistry has a long history and continues to be highly active, with new compounds discovered daily. By contrast, the area of two-dimensional (2D) materials is young, but its expansion, although rapid, is limited by a severe lack of structural diversity and complexity. Here, we report a novel 2D semiconductor with a hierarchical structure composed of covalently linked Re₆Se₈ clusters. The material, a 2D structural analogue of the Chevrel phase, is prepared via mechanical exfoliation of the van der Waals solid Re₆Se₈Cl₂. Using scanning tunneling spectroscopy, photoluminescence and ultraviolet photoelectron spectroscopy, and first-principles calculations, we determine the electronic bandgap (1.58 eV), optical bandgap (indirect, 1.48 eV), and exciton binding energy (100 meV) of the material. The latter is consistent with the partially 2D nature of the exciton. Re₆Se₈Cl₂ is the first member of a new family of 2D semiconductors whose structure is built from superatomic building blocks instead of simply atoms; such structures will expand the conceptual design space for 2D materials research.

KEYWORDS: Superatomic crystals, 2D semiconductor, exciton binding energy, van der Waals solid

The family of 2D materials includes the semimetal graphene, semiconducting transition metal dichalcogenides (TMDCs), and insulating hexagonal boron nitride (h-BN). Such materials have received widespread attention due to their novel 2D properties that are distinct from their bulk counterparts. Because of poor dielectric screening in the 2D geometry and quantum confinement, electronic excitations in these materials are excitonic in nature. These unique properties offer new possibilities for fundamental research and for diverse applications in electronics, optoelectronics, and valleytronics.

Nearly all 2D materials to date are atomic solids with relatively simple crystal structures. For example, graphene and h-BN consist of a single layer of atoms, and each TMDC is composed of a monolayer of transition metal atom sandwiched between two layers of chalcogen atoms. Beyond these simple lattices, there is a growing interest in designing 2D materials with complex, hierarchical, or tunable structures. In this context, cluster materials are attractive targets due to their synthetic flexibility and their exciting optical, electronic, and magnetic properties that derive from the cluster units. Despite the remarkable bulk properties of cluster materials, some of which have layered van der Waals structures, however, the lack of covalent bonding between the superatoms prevents their exfoliation down to few layers.

In this report, we investigate Re₆Se₈Cl₂, a van der Waals material derived from the Chevrel phase in which [Re₆Se₈] clusters are covalently linked into layers capped by terminal Cl atoms. We show that the strong in-plane intercluster bonding and weak interlayer interactions allow mechanical exfoliation, and their stability under ambient conditions offers additional benefits. Re₆Se₈Cl₂ was first reported in 1983 by Sergent and co-workers, but little is known about its electronic properties (e.g., the 2D nature of the band structure and associated strong excitonic effect). To better understand these properties, we carry out scanning tunneling microscopy/spectroscopy (STM/STS) measurement, combined with photoluminescence spectroscopy (PL) and ultraviolet photoelectron spectroscopy (UPS), on freshly cleaved Re₆Se₈Cl₂ crystals. The experimental findings are supported by density functional theory (DFT) calculations on both bulk and monolayer Re₆Se₈Cl₂. We find that bulk Re₆Se₈Cl₂ is an indirect bandgap material with the

Supporting Information

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valence band maximum (VBM) located at the Γ point, and the conduction band minimum (CBM) at the T point in momentum space. STS and PL spectroscopy reveal an electronic bandgap of 1.58 ± 0.03 eV and an optical bandgap of 1.48 ± 0.01 eV, respectively. We thus deduce a large exciton binding energy of ~100 meV.28,29 On the basis of STS characterization of atomic-scale defects and DFT calculations, we suggest that Cl vacancies are midgap states and are responsible for n-type doping.

All measurements are performed on single crystals of Re₆Se₈Cl₂ grown by chemical vapor transport. The material is first synthesized as microcrystalline powder by heating a stoichiometric mixture of Re, Se, and ReCl₅ to 1100 °C in a fused silica tube sealed under vacuum. Millimeter-sized single crystals are then grown by chemical vapor transport in a temperature gradient of 970–920 °C in the presence of a small excess of ReCl₅ as the transporting agent (see Synthetic Details). The structure of isolated crystals is determined by single crystal X-ray diffraction (SCXRD), and the phase purity of each sample is confirmed by powder X-ray diffraction (PXRD) (Figure S1). The Re₆Se₈Cl₂ lattice is built from isolated Re₆ octahedra enclosed in Se₈ cubes. Each cluster unit is linked to four neighbors in the basal plane through strong Re₂Se₂ bonds and is capped by two terminal Cl atoms in the apical positions (Figure 1a). The layers are pseudosquare lattices of tilted clusters, with lattice parameters a = 6.60 Å, b = 6.64 Å, and γ = 93.6°.26,30 The lattice parameter normal to the layers is c = 9.07 Å.

Our initial attempts at mechanical exfoliation using the Scotch tape method produced rectangular flakes as thin as ~15 nm, as determined by atomic force microscopy (AFM) (Figure 1b). Experiments to prepare Re₆Se₈Cl₂ monolayers are challenging and are presently underway. Here, we focus on the 2D semiconducting properties of multilayer Re₆Se₈Cl₂ flakes and bulk samples by performing measurements on freshly exfoliated surfaces.

We determine the optical gap of Re₆Se₈Cl₂ by optical absorption and PL spectroscopies. By combining white light transmittance and reflectance measurements of thin flakes on transparent substrates, we numerically solve for the refractive index and extinction coefficient. Figure 2a (red) presents the resulting absorption spectrum. The onset of absorption gives an optical gap $E_{\text{OG}} = 1.49 ± 0.02$ eV, in agreement with the PL spectrum peak at $E_{\text{OG}} = 1.48 ± 0.01$ eV. The experimentally determined real and imaginary parts of the dielectric function are in Figure S2. The valence band structure of the synthesized Re₆Se₈Cl₂ crystals are mapped out by UPS, Figure 2b, the onset of which gives a valence band maximum (VBM) at $E_{\text{VBM}} = 1.45 ± 0.01$ eV below the Fermi level ($E_F$). This places $E_F$ close to the conduction band minimum (CBM), implying that Re₆Se₈Cl₂ is an n-type semiconductor, in agreement with an early report based on electrochemistry27 and our STS measurements discussed below.

The temperature-dependent PL spectra in Figure 2c indicate that the bandgap of Re₆Se₈Cl₂ is indirect. The PL intensity increases with increasing temperature over the broad temperature range of 80–300 K. The plot of PL intensity as a function of temperature confirms that PL emission is thermally activated with an activation energy of 42.2 ± 1.4 meV (Figure S3). This is consistent with a radiative recombination mechanism in an indirect-bandgap semiconductor where phonons provide the necessary momentum conservation.

The indirect bandgap is confirmed by density functional theory (DFT) calculations. We calculate the band structure of

Figure 1. Crystal structure and exfoliation of the 2D van de Waals solid Re₆Se₈Cl₂. (a) Side view (top) of the ab plane and top view (bottom) of a single layer. Color code: Re, blue; Se, red; Cl, green. (b) Exfoliated Re₆Se₈Cl₂ flakes on SiO₂/Si. The height profile in red (insert) shows the thickness of a ~15 nm thin flake.

Figure 2. Electronic structure from spectroscopies and first-principles calculations. (a) Optical absorption (red) and photoluminescence (black) spectra of Re₆Se₈Cl₂. The onset of absorption spectrum at 1.49 ± 0.02 eV agrees with the PL peak position at 1.48 ± 0.01 eV. (b) Ultraviolet photoemission spectrum of Re₆Se₈Cl₂ showing the VBM at 1.45 eV below $E_F$. (c) Temperature-dependent PL of Re₆Se₈Cl₂ showing an increase in PL intensity with increasing temperature, suggesting an indirect bandgap. (d) Calculated DFT band structure with FBE-SOC (solid black line) and HSE06-SOC (blue dots).
Re$_6$Se$_8$Cl$_2$ on the experimental geometry by using the Perdew–Burke–Ernzerhof (PBE) functional$^{31}$ and refine the calculation with the Heyd–Scuseria–Ernzerhof (HSE06) functional,$^{32}$ both including spin–orbit coupling (SOC). Figure 2d shows the PBE-SOC band structure (black curves) and HSE06-SOC refinements at selected high-symmetry $k$ points (blue dots). The HSE06-SOC band structure gives an indirect bandgap of $E_G = 1.49 \text{ eV}$ between the VBM at $(0, 0, 0)$ and the conduction band minimum (CBM) at $(0, 0.5, 0.5)$. Compared to the results at the PBE-SOC level, HSE06-SOC mainly affects the valence band, down-shifting the VBM energy by $\sim 0.4$ eV with respect to that calculated with PBE-SOC. The computational results support the observed indirect bandgap and are in nearly quantitative agreement with the measured bandgap from STS, as detailed below.

We characterize the structure of the 2D plane of Re$_6$Se$_8$Cl$_2$ using STM. Figure 3a shows an STM image at room temperature. The surface is ultraflat with average roughness of only 0.4 Å; see also Figure S4 for large area AFM images. The inset in Figure 3a shows a step height of 8.9 Å along the red line, in agreement with the monolayer thickness determined by SCXRD. A high-resolution STM image, Figure 3b, reveals the pseudo-4-fold symmetry of the image, as suggested by the apparent off-centered position of the Cl atoms. A Fourier transform of the image (inset in Figure 3b) identifies the pseudo-4-fold symmetry of the 2D lattice plane.

We determine the single-particle band structure by current-voltage ($I$–$V$) measurement in STS. Figure 3d displays $I$–$V$ (blue) and $dI/dV$–$V$ (red) curves acquired on a cleaved Re$_6$Se$_8$Cl$_2$ surface. Each $I$–$V$ or $dI/dV$–$V$ curve is an average over 100 curves under the same tunneling conditions. We determine the positions of the VBM and CBM by taking the logarithm of $dI/dV$ (see details in Figure S5). The VBM is located at $-1.50 \pm 0.03$ V and the CBM at $+0.08 \pm 0.01$ V. These give the electronic bandgap $E_G = E_{\text{CBM}} - E_{\text{VBM}} = 1.58 \pm 0.03$ eV. The positions of the band edges relative to $E_F$ confirm n-doping.

On the basis of the optical bandgap and the electronic bandgap, we calculate an exciton binding energy of $E_B = E_G - E_{\text{VBM}} = 100 \pm 30$ meV, which is one order of magnitude larger than typical values in conventional 3D semiconductors (e.g., Si, Ge)$^{33,34}$ but comparable to that in a typical 2D van der Waals layered semiconductor such as MoS$_2$. To put the measured $E_B = 100 \pm 30$ meV value in perspective, we calculate the exciton binding energies based on a 3D or a 2D Bohr model.$^{35}$ We use the effective electron and hole masses ($m_e^*$ and $m_h^*$, respectively) from the PBE-SOC band structure in high symmetry directions: $m_e^* = 0.66m_e$ (in the $\Gamma$–$V$ or $\Gamma$–$X$ direction) and $m_h^* = 1.15m_e$ (in the $T$–$V$ or $T$–$X$ direction); $m_e$ is the free electron mass. On the basis of the exciton reduced mass $\mu = 1/(m_e^{*^{-1}} + m_h^{*^{-1}})$ and the measured dielectric constant $\varepsilon_r \approx 10.5$ at $\sim 1.5$ eV (Figure S2), we calculate exciton binding energies: $E_B^{3D} = \frac{\mu c^2}{2\hbar^2 \varepsilon_r n} = 50$ meV in 3D and $E_B^{2D} = \frac{\mu c^2}{2\hbar^2 \varepsilon_r n^2} = 200$ meV in 2D, where $n = 1$ for the ground excitonic state. The experimental binding energy $E_B = 100 \pm 30$ meV is between these two limiting values and suggests a partial 2D nature of excitons in Re$_6$Se$_8$Cl$_2$. This is expected from a 2D layered van der Waals structure with weak interlayer electronic coupling.

Having established the band structure of Re$_6$Se$_8$Cl$_2$, we now turn to the electronic properties of defects and the origin of n-doping. We characterize defects on the surface of Re$_6$Se$_8$Cl$_2$ by...
Figure 4. Defects on the Re₆Se₈Cl₂ surface. (a) STM image of a Re₆Se₈Cl₂ surface showing point defects marked by the blue arrows (32 × 32 nm, U = 0.6 V, I = 100 pA). The inset is a high-resolution image of a single defect. (b) dI/dV spectrum collected on top of the defect circled in panel a, showing a midgap state at ~0.67 V. (c) Real space plot of the HOMO of a single neutral on the 2D sheet, indicating the localization of unpaired electron on the Re site. (d) Log(PDOS) of the neutral Cl vacancy on the 2D sheet system, as calculated using HSE06-SOC.

STM/STS, in combination with DFT calculations. Figure 4a shows an atomic resolution image with defects appearing as dark spots at positive bias voltage (marked by blue arrows). The density of surface defects is ~1.5%, as determined by STM. The inset shows an individual defect with apparent depth and width about 1.0 and 8 Å, respectively, consistent with Cl vacancies (Figure S6). The loss of an electronegative atom from a polar semiconductor is expected to result in n-doping, as is also known for S vacancies in MoS₂. The inset shows a midgap state at 0.67 V. (c) Real space plot of the HOMO of a single neutral on the 2D sheet, indicating the localization of unpaired electron on the Re site, as illustrated in the real space plot of the highest molecular orbital (HOMO) of the neutral Cl vacancy on the 2D sheet (Figure 4b).

The results presented in this work establish Chevrel-type Re₆Se₈Cl₂ as the first member of the 2D hierarchical semiconductor family. An obvious research direction is to optimize the exfoliation method to reach the monolayer limit and these efforts are underway in our laboratories. Our calculations at the HSE06-SOC level reveal that the bandgap of Re₆Se₈Cl₂ increases from 1.49 eV in the bulk to 1.72 eV at the monolayer limit and remains indirect (Figure S9). Compared to other 2D materials, the uniquely complex structure of Re₆Se₈Cl₂ offers stimulating prospects for designing multiple functions and studying novel properties. The presence of substitutional labile Cl atoms on the surface of each Re₆Se₈Cl₂ layer opens the door to surface functionalization via substitution chemistry, which could allow tuning of the electronic structure. Moreover, the limited intercluster electronic coupling within each layer produces an electronic structure with narrow bandwidth (≤0.5 eV in Figure 2d), which is expected to be highly sensitive to phonon modes arising from the collective motions of the “superatomic” units. The 2D hierarchical structure of Re₆Se₈Cl₂ is thus an intriguing model system for investigating strong electron–phonon coupling and related electronic phase transitions.

Synthetic Details. A mixture of Re (330 mg, 1.7 mmol), Se (190 mg, 2.4 mmol), and ReCl₅ (200 g, 0.5 mmol) was intimately ground in an inert atmosphere, pressed into a pellet, and sealed in a quartz tube under vacuum. The sample was heated to 1100 °C with a ramp of 1 °C/min and held at 1100 °C for 3 days. The reaction took place in the presence of ReCl₅ vapor that was maintained by the addition of slight excess of Re and ReCl₅. Large single crystals of mm scale can be grown by subsequent chemical transport using ReCl₅ as the transport reagent with a temperature gradient of 970–920 °C. Large crystals are deposited at the cooler end of the tube. Before opening the sealed tube, the excess ReCl₅ that were deposited on the crystals was removed by condensing it to the cooler side of the tube by maintaining the tube under a temperature gradient of 300–25 °C for about 3 h.

Absorption/PL. Transmittance and reflectance spectra on thin films were collected and converted to absorption spectrum. Thin film samples were prepared by mechanically exfoliating the single crystals of Re₆Se₈Cl₂ and then characterized with AFM. Two different white light sources were used to measure ~30 nm thin samples with 40X objectives. Transmitted and reflected lights were collected and spectrally resolved with a Princeton Instruments PhotonMAX EMCCD camera.

Photoluminescence spectra were taken on bulk Re₆Se₈Cl₂ crystal. Crystals were cleaved before mounting onto a cryostat to achieve clean surface. 100 W/cm² 532 nm CW laser was illuminated on a crystal and the emission from sample was collected with Princeton Instruments PyLoN-IR InGaAs camera. The sample was first cooled with liquid nitrogen, and
spectra were acquired at temperature from 80 to 300 K (room temperature) in increments of 20 K.

**UPS.** Measurements were carried out on cleaved Re$_6$Se$_8$Cl$_2$ crystals with 39 eV extreme UV (XUV) radiation at room temperature. Freshly cleaved samples were transferred into an ultrahigh vacuum chamber ($\sim 10^{-10}$ Torr) where it was further annealed at 200 °C for 4 h. The XUV radiation for photoemission was obtained from high harmonic generation in Ar, with a commercial ultrafast extreme UV source (KMLabs, XUUS) pumped by the fundamental laser output from a Ti: sapphire amplifier (KMLabs, Wyvern, 5W, 40 fs, 10 kHz). The 25th harmonic output at 39 eV was selected with a grating downstream and applied for UPS measurements downstream. The XUV radiation was focused to a spot size of $\sim 150 \mu m$ with a spectral width of approximately 500 meV. The kinetic energy of the photoemitted electrons was measured using a hemispherical electron energy analyzer equipped with a 2D delay line detector (SPECS Phoibos-100).

**STM/STS.** We carried out experiments on freshly cleaved Re$_6$Se$_8$Cl$_2$ crystals using the Omicron scanning tunneling microscopy at room temperature (292 K) in an ultrahigh vacuum (base pressure $<4 \times 10^{-10}$ mtorr). Although we did not determine the exact thickness of the samples used in STM/STS, we estimated that they were thicker than those used in optical absorption spectroscopy ($\sim 30$ nm), as judged from optical images. We obtained the STM images in the constant-current mode with an electrochemically etched tungsten tip. To avoid tip artifacts, the STM tip was calibrated on a clean Au(111) surface before all measurements. We obtained differential conductance (dI/dV) spectra using a lock-in amplifier at an AC modulation of 10 mV and at a frequency of 891.1 Hz. The corresponding current change was acquired by keeping the tip fixed above the surface with the feedback loop off. dI/dV spectra were consistent at various spots on the surface with different tips at the same tunneling conditions and from different crystals.

**Computational Details.** DFT calculations were performed on the pristine 3D bulk (periodic boundary conditions) and 2D single sheet of Re$_6$Se$_8$Cl$_2$ by modeling both the pristine and Cl defective systems, that is, V$_{CI}$ in the supercell approach. The equilibrium structures of the 3D bulk pristine and defective systems were found by relaxing ions positions while keeping the cell parameters fixed to the experimental values: $a = 6.598 \text{Å}$, $b = 6.640 \text{Å}$, $c = 9.071 \text{Å}$, $\alpha = 100.19^\circ$, $\beta = 113.52^\circ$, and $\gamma = 93.64^\circ$. The 2D systems were modeled by fixing parameters $a$ and $b$ to the lattice constant and enlarging the cell along $c$ with a vacuum layer of 12 Å. The V$_{CI}$ defective system was investigated both in the bulk by modeling the vacancy in a $2 \times 2 \times 2$ supercell and on the 2D sheet by creating the vacancy in the $2 \times 2$ supercell.

Geometry relaxations were performed by using the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional,$^2$ plane waves basis set, and ultrasoft pseudopotentials. A cutoff on the wave functions of 40 Ryd (320 Ryd on the charge density) and converged Monkhorst–Pack grids of $k$ points in the BZ were used. For all investigated systems, structures were relaxed until forces acting on ions were less than 0.001 Ryd/Å. The electronic structures were then refined by using the hybrid HSE06 exchange correlation functional$^3$ including the spin–orbit interactions. Hybrid calculations were performed on the equilibrium structures optimized by PBE by using norm-conserving pseudopotentials with a cutoff on the wave functions of 70 Ryd. All calculations were carried out by using the Quantum Espresso software package.$^9$

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