Direct Observation of Li Migration into V₅S₈: Order to Antisite Disorder Intercalation Followed by the Topotactic-Based Conversion Reaction

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ABSTRACT: Two-dimensional transition-metal dichalcogenides hold great potential in rechargeable lithium-ion batteries. Their electrochemical properties are closely related to the structural evolutions during lithium-ion migration. Understanding these migration/reaction mechanisms is important to help improve battery performance. Herein, we report the real-time and atomic-scale observation of phase transitions during the lithiation and delithiation for V₅S₈ via in situ electron diffraction and high-resolution transmission electron microscopy techniques. We find that the phase transformation proceeds via a sequence of order to antisite disorder intercalation and topotactic-based conversion reaction. During the intercalation reaction, the lithium ion destroys the orderings of the interstitial V with the formation of Li/V antisite. Such a reaction is found to be reversible, i.e., the extraction of lithium from LiᵥV₅S₈ leads to the recovery of V orderings. The conversion reaction involves heterogeneous nucleation of Li₂S with 3−20 nm nanodomains, which maintain the crystallographic integrity with LiᵥV₅S₈. These findings elucidate the complex interactions between the lithium ion and host V₅S₈ during ionic migration in solids, which should be helpful in understanding the relationship between phase transformation kinetics and battery performance.

KEYWORDS: in situ TEM, transition-metal chalcogenide, lithium-ion migration, Li/V antisite, topotactic growth of Li₂S

1. INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have been used as an energy efficient storage device in portable electronics and electric vehicles.¹−³ The ever-growing demand for unique applications such as ultrafast discharging−charging, super large capacities, and high output power necessitates searching and developing new electrode materials. Transition-metal dichalcogenides (TMDs) have been extensively explored as promising anodes in LIBs due to their two-dimensional (2D) layered stacking structure through weak van der Waals interactions, which facilitates the fast alkaline ions transport.⁴ These TMDs have demonstrated good Li-storage capacities via complex reactions including intercalation, conversion, and alloying reaction.⁷−¹⁰ It is reported that the inserted lithium ions trigger different phase transformations via different pathways, such as 2H to 1T transition in MoS₂,¹¹−¹³ disordering transition¹⁴ and intermediate superstructure¹⁵ in SnS₂, twophase transition in TiS₂,¹⁶−¹⁸ metal extrusion in CuS₂,¹⁹ and anisotropic lithiation in ReS₂.²⁰ These diverse lithiation pathways generate different intermediate or final products, which in turn influence the reaction reversibility, energy efficiency, and battery cyclability.²¹,²² Therefore, it is important to investigate the reaction pathway and phase transformation to improve battery performance.

Metallic VS₂ has a large interlayer spacing of 5.67 Å,²³ which processes a high energy density and good reversibility as an anode material for LIBs.²⁴,²⁵ V₅S₈ is another member of vanadium sulfides family that consists of ordered V within the interlayers, occupying one-quarter of available S−S octahedral sites and linking the two adjacent VS₂ monolayers. Such a three-dimensional structure can overcome the drawback of a 2D structure with anisotropic diffusion, which requires more engineering to align the crystal planes with the diffusional direction to achieve large insertion efficiency.²⁶ Moreover, the metallic nature of V₅S₈ is beneficial to the transport of electrons. These aspects enable V₅S₈ to be used in not only Li but Na and K ion batteries with good electrochemical performance.²⁷−²⁹ For example, V₅S₈/C delivers high discharge and charge capacity of 1245 and 1112 mAh g⁻¹ at 0.1 A g⁻¹ and the capacity is maintained at 846 mAh g⁻¹ after 700 cycles at 1 A g⁻¹ for LIBs. With the current density increased
to 8.0 A g⁻¹, the specific charge capacity can maintain at 432 mAh g⁻¹ and recovers to 821 mAh g⁻¹ when the rate returns to 0.1 mAh g⁻¹. Ou et al. studied the electrochemical reaction mechanism of V₅S₈ and its reversibility during the electrochemical cycling by in/ex situ X-ray diffraction (XRD). During the discharge, they observed an intercalation reaction to form LiₓV₅S₈ from open-circuit voltage to 0.45 V, followed by a conversion reaction to form Li₂S and V from 0.45 to 0.01 V. At the charge process, LiₓV₅S₈ is formed from 0.01 to 1.7 V and the structure is restored to V₅S₈ from 1.7 to 3.0 V. However, how the ions react with the host atoms and migrate within V₅S₈ and how the reaction interface evolves, which are related to the electrochemical performance, have been rarely explored, thus motivating our study.

In this work, using in situ electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) techniques, we have tracked the dynamical structural evolutions during the (de)lithiation of V₅S₈ from nanometer to an atomic scale. We find that the initial insertion of lithium ions is via an intercalation reaction, which triggers an order to antisite disorder transformation by destroying the orderings of the interstitial V. Such transition is found to be reversible, i.e., the extraction of lithium ions from LiₓV₅S₈ results in the recovery of the orderings of interstitial V atoms. The following...
conversion reaction involves the heterogeneous nucleation and topotactic growth of Li2S nanodomains. These findings reveal detailed structural evolutions during lithium migration in V5S8, indicating delicate and complex interactions between foreign ions and host atoms rather than a simple van der Waals interaction that may exist in TMD electrode materials.

2. RESULTS AND DISCUSSION

Figure 1a shows a typical schematic diagram of a nanosized solid battery to achieve (de)lithiation, including a Li counter electrode, a solid-state electrolyte (a passivation Li$_x$O layer), and a V$_5$S$_8$ nanosheet as the working electrode. The V$_5$S$_8$ nanosheet is thinned from the bulk (Figure S1), which is synthesized by a chemical vapor transport method, as we have previously reported. V$_5$S$_8$ is composed of distorted VS$_2$ layers intercalated with ordered V atoms, which occupy one-quarter of the octahedra sites (Figure 1a). Such interstitial V atoms cause superstructure diffraction spots (Figure 1b), compared with that of VS$_3$ (Figure S2). The acquired high-angle annular dark-field-scanning TEM (HAADF-STEM) image in Figure 1c is consistent with the atomistic structure along the [001] rather than the [100] zone axis despite their ED patterns being quite similar (Figure S3). The bright and dark atom columns are identified as V and S, respectively. Upon lithium insertion, a clear phase boundary between Li$_x$V$_5$S$_8$ and V$_5$S$_8$ can be observed, as shown in Figure 1d and Movie S1. As the lithiation progresses, the reaction gradually propagates from the surface to internal. We further acquire the diffusivity of the lithium ion (Figure 1e), according to the equation $D = d^2/2t$, where $D$ is the diffusivity, $t$ is the diffusion time, and $d$ is the diffusion distance. The measured diffusivity is based on the migration of the reaction front, indicating the lithium diffusion in V$_5$S$_8$. The calculated diffusivity is about $10^{-13}$–$8 \times 10^{-13}$ cm$^2$ s$^{-1}$, which is comparable to the electrochemically measured diffusivity ($6.168 \times 10^{-13}$–$8.285 \times 10^{-13}$ cm$^2$ s$^{-1}$). The valley at 100 s is likely caused by the change of a worse contact between Li$_2$O and V$_5$S$_8$. More accurate Li diffusion coefficients in different phases can be obtained by the galvanostatic intermittent titration technique.

To investigate the structural evolutions during lithium ions intercalation, we carried out time-series in situ electron diffraction experiments, as shown in Figure 2a–d and Movie S2. The SAED pattern (Figure 2a) indicates a good single crystalline structure of V$_5$S$_8$. Upon the insertion of lithium ions, we observe that the superstructure diffraction spots gradually disappear (Figure 2b). The superstructure reflections are caused by ordered interstitial V atoms; thus, its disappearance suggests that such periodic interstitial V arrangement is damaged and all octahedral sites within the interlayer are randomly occupied by lithium or V, as illustrated in Figure 2e–f. The crystal symmetry of V$_5$S$_8$ is monoclinic (space group: P2$_1$/m), while Li$_x$V$_5$S$_8$ with disordered V is hexagonal (space group: P3$m1$). The simulated ED pattern of such a Li/V random structure can match with experimental one (Figure S4). In contrast, the superstructure can be maintained for 2 h under the pure electrical field (Figure S5 and Movie S3), further suggesting that the disappearance of the superstructure is not caused by the electrical field and the electron beam irradiation at low doses but related to lithium insertion. With more lithium ions insertion, we observe the formation of Li$_2$S (JCPDS No. 23-36322).
Volume expansion. The di... are extracted in Figure 2h, presenting the whole... reaction to form Li2S and V. The corresponding reaction equations can be expressed as

\[ \text{conversion: } \text{Li}_x\text{V}_5\text{S}_8 + (16 - x)\text{Li}^+ + e^- \rightarrow 8\text{Li}_2\text{S} + 5\text{V} \]

The overall reaction mechanism is similar to previous in situ XRD results\(^{34}\) that are initiated from intercalation and followed by a conversion reaction. However, our in situ TEM experiments provide more microscopic structural insights that the inserted lithium ions can destroy the orderings of the interstitial V and the formed Li2S maintains the crystallographic integrity with Li\(_x\)V\(_5\)S\(_8\). To further reveal local structural evolutions, time-series HRTEM images are recorded in Figure 3a–h. Figure 3a is a typical HRTEM image of V\(_5\)S\(_8\) viewing along the [001] direction. Due to the orderings of interstitial V atoms, the pristine V\(_5\)S\(_8\) features superstructure stripes (Figure 3e) and diffraction spots (Figure 3i). Upon the lithium insertion, such superstructure stripes and diffraction reflections disappear and the corresponding plane distance (2.85 Å) (Figure 3b,f,j) becomes one-half of the pristine one (5.71 Å), indicating the loss of the orderings of interstitial V. We can observe the intercalation interface between V\(_5\)S\(_8\) and Li\(_x\)V\(_5\)S\(_8\) as well as the formation of Li\(_2\)S nanodomains (Figure 3b). The priority to forming the Li\(_2\)S (220) plane is again observed (Figure 3c,g,k). Interestingly, we find heterogeneous nucleation of Li2S during the conversion reaction marked by the yellow circles in Figure 3b,c. The size of Li2S nanodomains ranges from 3 to 9 nm near the reaction front and grows larger away from the reaction front (12–18 nm). From the enlarged view of a small Li\(_2\)S domain (Figure 3g), we can observe that the clear lattice stripes of the Li\(_2\)S (220) plane maintain a topotactic relationship with the Li\(_x\)V\(_5\)S\(_8\) (400) plane. These small Li2S domains grow larger and larger, and finally, the structure totally transforms into Li\(_2\)S (Figure 3h,i). Note that Li\(_2\)S nanodomains are formed near the interface (Figure 3b,c) between the pristine V\(_5\)S\(_8\) and Li\(_x\)V\(_5\)S\(_8\), which suggests that bulk V\(_5\)S\(_8\) is partially inserted and then converted rather than fully intercalated and then converted. Such nonequilibrium lithiation has also been observed in Fe\(_2\)O\(_4\)\(^ {35}\) and Co\(_3\)O\(_4\)\(^ {34}\) nanoparticles, which is influenced by discharging rates. At a low rate, the conversion reaction starts after the full intercalation while the intercalation reaction can be overwhelmed by the conversion reaction at a high rate.\(^ {34}\) Accordingly, an effective controlling the degree of the lithiation can be achieved by regulating the discharging rate for these intercalation-conversion-type electrode materials.

For rechargeable LIBs, it is a prerequisite to reversibly insert lithium ions into host materials. We find that once the insertion of lithium ions into V\(_5\)S\(_8\) is controlled within the intercalation range, the lithium ions in Li\(_x\)V\(_5\)S\(_8\) can be partly extracted (Movie S4). We first insert lithium ions into V\(_5\)S\(_8\) by...
applying a −2 V voltage. Upon lithium insertion, the superstructure diffraction spots gradually disappear (Figure 4a,b). Though the zone axis has changed a little (Figure 4a,b), the zone axis tilting effect on the disappearance of superstructure spots can be eliminated, as explained in Figure S8. Once the diffraction spots of Li2S appear (Figure 4b), indicating the conversion reaction starts, the applied voltage is changed to be +4 V to extract the lithium ions in Li1V5S8. It is found that the disappeared superstructure reflections gradually reappear (Figure 4c,d), suggesting that the random V becomes ordered due to the extraction of lithium ions. Such reversible intercalation reaction, as illustrated in Figure 4e,f, can promise good cycling performance when lithiation is controlled within the intercalation range, which has been used to improve the cycling performance of VS2.36

It is known that the battery performance is largely determined by the structural evolutions during the reaction for LIBs. By in situ TEM, we investigate the reaction pathways and phase transformations of V5S8. During the lithiation of V5S8 we find the orderings of the interstitial V is destroyed since the inserted lithium can take up the position of interstitial V and pull V to the neighboring octahedral sites due to Coulomb repulsion,37 enabling Li and V to occupy the octahedral sites randomly. Indeed, the interstitial V in V5S8 can migrate to the near octahedral sites above 800 °C, transforming into a CdI2-type structure.32 Then, the octahedral sites within S−V−S layers become equivalent and vacancies and cations become randomly distributed, leading to a symmetry change from F2/m to P3m1.33 The previous work reported that the ordered Na/vacancy superstructure within the interlayers in NaCoO2 lowers Na diffusion coefficient even up to two orders of magnitude.38 Based on the first-principles calculations, we also compare the diffusion barriers of lithium diffusing in the bulk VS2 (without ordered V within the interlayers) and V5S8 (existing ordered V within the interlayers). The lithium diffusion barriers are about 0.26 eV in VS2 and 0.42 eV in V5S8, as shown in Figure S9. The lower diffusion barrier in VS2 suggests a fast lithium-ion diffusion, which is consistent with the electrochemical measurements that the lithium-ion diffusion coefficient in V5S8 (6−8 × 10−13 cm2 s−1)28 is 2−3 magnitude lower than that for VS2 (10−10−10−12 cm2 s−1).39 Accordingly, the ordered V might generate a higher diffusion barrier that blocks the diffusion of lithium, and such a V disordered structure is likely beneficial to the diffusion of lithium.

To further confirm such disordering behavior at an atomic scale, we have mimicked the superstructure-nonsuperstructure transition under the high-energy electron beam, which has been widely used to track the dynamics of the phase transition.40,41 Figure 5a is an atomically resolved HAADF-STEM image of the pristine V5S8. After beam illumination (see the Experimental Section for details), the superstructure lattices disappear with the plane distance becoming half of the pristine value (Figure 5a,b), accompanying with the disappearance of the superstructure reflections (Figure 5c,d). It is found that the uneven contrast of each atom column (Figure 5e) becomes more uniform (Figure 5f) after beam irradiation. In fact, the uneven contrast is caused by the interstitial V, which brings in a brighter contrast, as verified in the corresponding simulated HAADF STEM image (Figure S10). Under electron beam illumination, similar to that under the heat,32 the interstitial V can migrate to the near equal octahedral sites; thus, vacancies and V become distributed randomly within this layer, leading to a uniform STEM contrast (Figure 5f).

Furthermore, our in situ TEM study has revealed a topotactic growth of Li2S during the conversion reaction of V5S8. The topotactic transition means that the crystal orientation of the product phase is correlated with the crystal orientation of the parent phase.42,43 The orientation of the substrate determines the crystal orientation of the product, thus influencing the nucleation and growth of a new phase considering that different orientations might have different nucleation energy and growth driving energy.44 Different from most topotactic transformations observed in the intercalation process via shuttling lithium ions between the tunnels of the host,45 we find a topotactic conversion transformation, which plays a vital role in understanding the structure evolutions and the related battery performance. It is reported the topotactic cation diffusion through an invariant lattice of fluoride anions...
governs the reversibility of the conversion reactions.\textsuperscript{42} However, most studies failed to observe such behavior due to material or technique restrictions. For example, the powder and the polycrystalline materials show random orientation\textsuperscript{18,46} preventing the identification of the specific orientation relationship. Also, in situ XRD techniques provide the information of a series of equivalent planes rather than one specific one. Thus, it is beneficial to clarify more information about such topotactic transformation by in situ TEM techniques of the single-crystal battery materials.

We also compare the reaction mechanism of V\textsubscript{5}S\textsubscript{8} with other TMDs. Similar to Mo\textsubscript{5}S\textsubscript{8}\textsuperscript{13} and TiS\textsubscript{2}\textsuperscript{16,17} the reaction process of V\textsubscript{5}S\textsubscript{8} proceeds via a sequence of intercalation and conversion reactions. The difference lies in the behaviors of the superstructures. The lithiation of MoS\textsubscript{2} and TiS\textsubscript{2} enables the formation of superstructures due to the distortion of Mo\textsubscript{11} or the ordered lithium insertion.\textsuperscript{10} V\textsubscript{5}S\textsubscript{8} itself shows the feature of Li\textsuperscript{+} superstructures due to the ordered interstitial V. Because of the Li−V interactions, the inserted lithium ions can destroy such V orderings with the disappearance of the superstructure. Similarly, the insertion of sodium into MoS\textsubscript{2} enables the formation of superstructure due to the ordered interstitial V. Of the Li−V interactions, the inserted lithium ions can destroy such V orderings with the disappearance of the superstructure. During the following conversion, heterogeneous Li\textsubscript{2}S nanodomains are formed, maintaining the crystallographic integrity with the Li\textsubscript{1}V\textsubscript{5}S\textsubscript{8}. The reversibility of the conversion reactions seems to be highly dependent on these Li\textsubscript{2}S nanodomains and its topotactic growth feature, which might guide future material research to develop and identify high-energy materials with a reversible conversion reaction. This mechanistic understanding of V\textsubscript{5}S\textsubscript{8} provides some insights for the intercalation-conversion type materials, which will guide the future development of high energy density materials.

3. CONCLUSIONS
In summary, we have investigated the lithiation mechanism of V\textsubscript{5}S\textsubscript{8} by in situ TEM at an atomic scale. It is found that the lithiation process is initiated with a cationic order-to-disorder intercalation and followed by a conversion reaction. The insertion of lithium can destroy the orderings of interstitial V atoms. The intercalation reaction is found to be reversible, and the lithium ions can be extracted from Li\textsubscript{1}V\textsubscript{5}S\textsubscript{8} accompanying by the recovery of the superstructure. During the following conversion, heterogeneous Li\textsubscript{2}S nanodomains are formed, maintaining the crystallographic integrity with the Li\textsubscript{1}V\textsubscript{5}S\textsubscript{8}. The reversibility of the conversion reactions seems to be highly dependent on these Li\textsubscript{2}S nanodomains and its topotactic growth feature, which might guide future material research to develop and identify high-energy materials with a reversible conversion reaction. This mechanistic understanding of V\textsubscript{5}S\textsubscript{8} provides some insights for the intercalation-conversion type materials, which will guide the future development of high energy density materials.

4. EXPERIMENTAL SECTION
4.1. Synthesis of V\textsubscript{5}S\textsubscript{8}. The bulk V\textsubscript{5}S\textsubscript{8} was synthesized by the chemical vapor transport method. The precursors (vanadium and sulfur powders) and transport agent (iodine) were first put into a silica ampule under argon. The ampule was then evacuated, sealed, and heated in a two-zone tube furnace to a temperature gradient of 850−1000 °C for 2 weeks before acquiring the bulk crystals.

4.2. In Situ TEM Experiments. In situ TEM experimental setup includes a V\textsubscript{5}S\textsubscript{8} working electrode, a lithium metal as the counter electrode, and a thin layer Li\textsubscript{1}O as the solid electrolyte. The formed Li\textsubscript{1}O can serve as a solid-state electrolyte that allows the transport of Li\textsuperscript{+} and prevents the transport of the electron since Li\textsubscript{1}O is a good Li\textsuperscript{+} conductor and an electronic insulator with the diffusivity of Li\textsuperscript{+} being 10\textsuperscript{−10} cm\textsuperscript{2} s\textsuperscript{−1} and a large band gap of ~8 eV.\textsuperscript{48} V\textsubscript{5}S\textsubscript{8} used in this work was prepared by the mechanical polishing and ion-beam milling process using argon ion milling (Leica EM RES102). The ion milling process was carried out at 5 kV until a hole appeared, and then a low voltage (0.8 kV) was used to reduce the irradiation-damaged layers.

The metal lithium was scratched using an electrochemically etched sharp tungsten tip. The electrical TEM specimen holder (PicoFemto) was sealed in an argon-filled glovebox and then transferred into the TEM column. During the transfer process, the lithium probe was exposed to the air to form Li\textsubscript{1}O on the surface. Basically, the exposure time was controlled within 5 s to obtain a 700−1000 nm Li\textsubscript{1}O layer.\textsuperscript{48} The tungsten tip is driven by a piezo-ceramic manipulator to contact with V\textsubscript{5}S\textsubscript{8}. The lithiation of V\textsubscript{5}S\textsubscript{8} was achieved by applying a small negative bias (−2 V) between the grounded tungsten probe and V\textsubscript{5}S\textsubscript{8}, while a positive bias (4 V) was employed to extract the lithium ions.

4.3. Characterizations and Analysis. Powder XRD pattern was obtained on D8 Advance diffractometer using Cu Kα radiation (40 kV and 100 mA), and the SEM image was acquired by FEI Quanta 200F. In situ ED and HRTEM techniques were carried out at a dose rate of 2 and 800 e Å\textsuperscript{−2} s\textsuperscript{−1}, respectively, using Tecnai F20 at 200 kV equipped with a OneView IS (Gatan) camera. The atomically resolved STEM images were acquired using an aberration-corrected FEI Titan Themis G2 microscope operated at an accelerating voltage of 300 kV with a beam current of 50 pA, a convergence semiangle of 21 mrad, and a collection semiangle snap in the range of 80−380 mrad. The electron beam irradiation experiment was carried out using the STEM area scanning mode at 100 pA with an 18 nm × 18 nm scanning area. The corresponding dose rate is estimated to be 1.92 × 10\textsuperscript{−6} e Å\textsuperscript{−2} s\textsuperscript{−1}.\textsuperscript{49} The movies were prepared from time-series images. FFT patterns and the line profiles were obtained using DigitalMicrograph (Gatan) software. The simulation of the ED patterns was performed using Crystalmaker software, and the atomic models were obtained by Vesta software. The radial intensity profiles are prepared by ImageJ software. The STEM simulation was carried out by Kirkland with COMPUTEM software.\textsuperscript{50} The plots were drawn using Origin 2016.

4.4. First-principles Calculations. The structures of the bulk V\textsubscript{5}S\textsubscript{8}, VS\textsubscript{3}, and their Li-adsorbed compounds were fully optimized by Vienna Ab initio Simulation Package (VASP).\textsuperscript{51} The climbing image nudged elastic band method was implemented in the VASP transition state tools to calculate the diffusion barriers of lithium ions.\textsuperscript{52,53} In our calculation, density functional theory with a cutoff energy of 500 eV was used; the generalized gradient approximation combined with the Perdew−Burke−Ernzerh form and the plane-wave basis set with the projector-augmented wave pseudopotential were adopted; the k-point mesh was sampled by the Monkhorst−Pack method with a separation of 0.02 Å\textsuperscript{−1}; and the convergence threshold were 10\textsuperscript{−5} eV for energy and 10\textsuperscript{−3} eV Å\textsuperscript{−1} for a force to get the precise results.\textsuperscript{54,55}

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c08428.

Structure and morphology of V\textsubscript{5}S\textsubscript{8}; comparison of V\textsubscript{5}S\textsubscript{8} and VS\textsubscript{3}; comparison of V\textsubscript{5}S\textsubscript{8} and Li\textsubscript{1}V\textsubscript{5}S\textsubscript{8}; structural evolutions under pure electrical field; plane distance changes during the lithiation of V\textsubscript{5}S\textsubscript{8}, formation of metal V; simulated ED patterns of V\textsubscript{5}S\textsubscript{8}; diffusion pathways and energy profiles; structure of V\textsubscript{5}S\textsubscript{8} along the [001] direction; unfiltered HAADFSTEM images (PDF)

Migration of phase boundary between Li\textsubscript{1}V\textsubscript{5}S\textsubscript{8} and V\textsubscript{5}S\textsubscript{8} (MP4)

Time-series in situ SAED patterns upon lithium ion insertion into V\textsubscript{5}S\textsubscript{8} (MP4)

Superstructure maintained for 2 h at a dose rate of 2 e Å\textsuperscript{−2} s\textsuperscript{−1} under the pure electrical field (MP4)

Time-series SAED patterns showing lithium ion interaction and extraction process (MP4)
performed SEM and XRD characterizations with the guidance of J.L.; J.N. grew the V5S8 crystals and in situ TEM experiments with the guidance of P.G. and help from R.S. and X.M.; C.Y. conducted the DFT calculations under the guidance of J.L.; J.N. grew the V5S8 crystals and performed SEM and XRD characterizations with the guidance from X.W.; M.W. prepared the TEM specimens. J.C., J.F., L.W., and J.Q. provided crystals. S.C., L.W., and P.G. wrote the manuscript, and all authors participated in the discussions.

**References**


