Metal–insulator transition tuned by magnetic field in Bi$_{1.7}$V$_8$O$_{16}$ hollandite†

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A metal–insulator transition tuned by application of an external magnetic field occurs in the quasi-one dimensional system Bi$_{1.7}$V$_8$O$_{16}$, which contains a mix of $S = 1$ and $S = 1/2$ vanadium cations. Unlike all other known vanadates, the magnetic susceptibility of Bi$_{1.7}$V$_8$O$_{16}$ diverges in its insulating state, although no long-range magnetic ordering is observed from neutron diffraction measurements, possibly due to the frustrated geometry of the triangular ladders. Magnetotransport measurements reveal that the transition temperature is suppressed upon application of an external magnetic field, from 62.5 K at zero field to 40 K at 8 T. This behavior is both hysteretic and anisotropic, suggesting $t_2g$ orbital ordering of the V$^{3+}$ and V$^{4+}$ cations drives a first-order structural transition. Single crystal X-ray diffraction reveals a charge density wave of Bi$^{3+}$ cations with a propagation vector of 0.846$c^*$, which runs parallel to the triangular chain direction. Neutron powder diffraction measurements show a first-order structural transition, characterized by the coexistence of two tetragonal phases near the metal–insulator transition. Finally, we discuss the likelihood that ferromagnetic V–V dimers coexist with a majority spin-singlet state below the transition in Bi$_{1.7}$V$_8$O$_{16}$.

1 Introduction

Vanadium oxides are well-known to exhibit metal-to-insulator transitions (MIT) and the underlying mechanisms can involve the ordering of charge, orbital, and/or spin degrees of freedom.1–9 A lingering question in these materials is whether Mott-type physics (i.e. electron–electron correlations) drive the MIT or whether Peierls-type interactions (i.e. electron–phonon interactions) are instead responsible.10–13 Furthermore, charge ordering seems to be a key ingredient in observing MITs such as in various β-vanadium bronzes and in NaV$_2$O$_5$, which undergoes charge ordering at 34 K.2,3,5–7 The study of vanadates with various geometries affords the opportunity to better separate the parameters responsible for MITs; the title compound Bi$_{1.7}$V$_8$O$_{16}$ contains a quasi-one dimensional (1D) geometry with a unique composition of $S = 1$ and $S = 1/2$ cations that allow such parameters to be better separated in order to shed light on similar systems.

Bi$_{1.7}$V$_8$O$_{16}$ belongs to the structural class of materials known as hollandites, which generally have the nominal formula of A$_x$M$_8$O$_{16}$, where $x \leq 2$. The A cation in hollandites is often nonstoichiometric and charge orders depending on its size and occupation. The A cation’s occupation and distribution therefore affects the oxidation state of the transition metal cation M, often resulting in a mixed valency of 3+ and 4+ states. The structure can be described as a square channel occupied by Bi$^{3+}$ cations, with walls composed of edge-sharing VO$_6$ octahedra (Fig. 1b). The V cations are arranged in triangular ladders (Fig. 1a). This topology, coupled with mixed valency, can lead to interesting properties including insulating ferromagnetism,14–16 frustrated magnetism,17–19 and MITs.20–22 The triangular ladder is known to lead to magnetic frustration such as in the hollandite Ba$_{1.3}$Mn$_8$O$_{16}$,18

Bi$_{1.7}$V$_8$O$_{16}$ exhibits an MIT close to 70 K, but unlike all other known vanadates that undergo MITs, the magnetic susceptibility...
of Bi$_{1.7}$V$_8$O$_{16}$ diverges upon entering the insulating phase.$^{1,4}$ Kato et al. first demonstrated that the divergence in the magnetization of Bi$_{1.7}$V$_8$O$_{16}$ is concomitant with the MIT near 70 K.$^{23}$ The uniqueness of this transition, however, was never investigated by structural or magnetotransport studies to explore whether the system was undergoing long-range magnetic ordering at the MIT, which would imply that Mott-type physics was playing a dominant role. Furthermore, whether or not the vanadium cations dimerize upon entering the insulating phase has been unresolved up to this point.

We aim to resolve whether the orbitally active V$^{4+}$ and V$^{3+}$ cations and their mixed spin states are responsible for the divergence in magnetization at the MIT and to understand how crystal structure and external magnetic field affect the transport properties. Understanding these questions would have implications on other vanadates with MITs. Our combined X-ray and neutron diffraction studies along with magnetotransport and magnetization measurements reveal important details regarding the nature of the charge, orbital, and spin states in Bi$_{1.7}$V$_8$O$_{16}$.

2 Experimental

We prepared polycrystalline and single crystal samples of Bi$_{1.7}$V$_8$O$_{16}$ hollandite. Powders were produced by grinding together stoichiometric ratios of V$_2$O$_5$ (99.7%, Alfa Aesar), V$_2$O$_3$ (98+%, Sigma Aldrich), and Bi$_2$O$_3$ (99%, Fisher). Reagents were used without further purification. After grinding together, the powdered mixture was pressed into a pellet and heated to 1173 K at a rate of three degrees per minute in an evacuated flame-sealed quartz glass ampule. Once the target temperature was reached, the sample soaked for 72 hours, followed by furnace cooling.$^{24}$

Needle-like single crystals of Bi$_{1.7}$V$_8$O$_{16}$ were grown by two different methods. One route includes using an excess of Bi$_2$O$_3$ during the solid state reaction followed by physical removal of crystals from the excess Bi$_2$O$_3$ flux. The other route includes mixing a KCl/NaCl salt mixture (1:1 molar ratio) with a pre-reacted powder mixture in an alumina crucible sealed in an evacuated quartz ampoule. The product: flux molar ratio was 1:10, and the mixture was heated to 1273 K for 10 hours, followed by slow cooling at 5 K h$^{-1}$. Flux was removed by washing with deionized H$_2$O.

Synchrotron XRD was collected at the 11-BM instrument at the Advanced Photon Source with $\lambda = 0.41397$ Å from 100 K to 300 K. Constant wavelength neutron powder diffraction data was collected on the high resolution BT-1 instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) with a $\lambda = 2.078$ Å (Ge311 monochromator) for various temperatures between 10 K and 300 K. All powder diffraction data was analyzed using the TOPAS software.$^{25}$

A black needle-like specimen of Bi$_{1.7}$V$_8$O$_{16}$ with approximate dimensions of 0.03 mm $\times$ 0.03 mm $\times$ 0.26 mm was used for single crystal X-ray diffraction (XRD) analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a Mo K$\alpha$ sealed tube ($\lambda = 0.71073$ Å). Full structures were taken at 90 K, 200 K, and 300 K, and partial measurements for lattice constant determination were taken between 90 K and 290 K in 20 K steps. At 200 K, integration of the data using a tetragonal unit cell yielded a total of 2244 reflections to a maximum $\theta$ angle of 32.42° (0.66 Å resolution), of which 299 were independent. The structure was solved and refined using the Bruker SHELXTL Software Package.$^{26,27}$

The final anisotropic full-matrix least-squares refinement on $P\overline{4}$ with 27 variables converged to a $R_I = 1.44\%$ for the observed data and $wR^2 = 3.70\%$ for all data.

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements were taken from 2–300 K with a Quantum Design magnetic property measurement system (MPMS) on a polycrystalline sample. Measurements were in direct current mode, with an applied magnetic field of 0.01 T (100 Oe). Magnetization versus field up to 7 T were also taken on the MPMS with a polycrystalline sample at 5 K. Transport measurements were taken in a Quantum Design physical property measurement system (PPMS). A four-probe geometry was used on both a sintered pellet and later on single crystals, to measure electrical resistance first upon cooling, then upon heating. For the single crystal measurements, magnetic fields were measured up to 8 T, with ramp rates of 1 T min$^{-1}$ in the temperature region of the MIT, and 5 T min$^{-1}$ above 100 K. Field was applied either along the needle direction, $H_\parallel$, or normal to it, $H_\perp$.

3 Results

3.1 Powder diffraction

To investigate the effects of the temperature-induced MIT on the structure of Bi$_{1.72}$V$_8$O$_{16}$, we performed temperature-dependent X-ray and neutron powder diffraction (NPD). Rietveld refinements were carried out to extract structural and lattice parameters from the data. Structural and lattice parameters for representative temperatures of the NPD data are gathered in Table 1.

Temperature dependent NPD data reveals Bi$_{1.7}$V$_8$O$_{16}$ to undergo a first-order tetragonal-to-tetragonal structural phase transition. While at 10 K and 300 K, far from the MIT, the crystal structure could be fit with a single tetragonal phase, close to the transition we noted significant peak splitting. Fig. 2 shows three NPD patterns of polycrystalline Bi$_{1.7}$V$_8$O$_{16}$ for the 40 K, 67.5 K, and 80 K temperature steps upon warming. As seen in the 67.5 K data, the NPD pattern is fit well to two tetragonal phases, with phase fractions tracking the transition from insulating to metallic behavior (Fig. 3). A similar tetragonal-to-tetragonal transition has been observed in Rb$_2$V$_8$O$_{16}$ at its MIT of 240 K,$^{28}$ whereas the MIT in K$_2$V$_8$O$_{16}$ (155–170 K) is accompanied by a structural distortion from tetragonal to monoclinic.

The most notable structural difference between the low-T (insulating) and high-T (metallic) phases is the significant expansion in the c-direction, which runs along the triangular ladders, upon entering the insulating phase. Temperature dependence

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$^2$ Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.
of the lattice parameters from all three different probes, neutrons, powder X-ray, and single crystal X-ray, are included in Fig. 4, though only our neutron measurements allowed us to investigate the structure below 90 K. The change in lattice parameters observed in Fig. 4 suggests that dimerization must occur along the \( c \)-direction rather than the \( ab \)-direction, and therefore that the V–V pair formation occurs along the triangular ladder sides rather than the ladder rungs (Fig. 1a).

Another notable result from the NPD data, is the lack of either magnetic or nuclear satellite reflections in the low-\( T \) phase. This result leads to the conclusion that no long-range magnetic order sets in during the MIT, and therefore electron–electron correlations leading to a Mott-type transition is unlikely. One must note, however, that the structure of the low-\( T \) phase may indeed be lower in symmetry than the tetragonal phase reported here since the NPD data cannot definitively prove this. Unfortunately, vanadium atoms do not strongly scatter neutrons, especially relative to the other elements in Bi\(_{1.7}\)V\(_8\)O\(_{16}\), with neutron scattering lengths of \( -0.443 \, \text{fm} \) for V, compared to 8.332 fm for Bi and 5.805 fm for O.\(^{29}\) The ramifications of this reality are that any satellite reflections arising from V cation displacements could be missed by the NPD measurements.

### Table 1  Structural parameters for Bi\(_{1.7}\)V\(_8\)O\(_{16}\) from NPD data taken at temperatures across the MIT

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Unit Cell</th>
<th>( R_{wp} )</th>
<th>( a ) (Å)</th>
<th>( c ) (Å)</th>
<th>( V ) (Å(^3))</th>
<th>Atom</th>
<th>Site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{iso} ) (Å(^2))</th>
<th>Occ.</th>
</tr>
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<tr>
<td>300 K, ( I4/m ), ( R_{wp} = 5.521% )</td>
<td>( b )-( c )-tetragonal</td>
<td></td>
<td>9.9243(1)</td>
<td>2.92301(5)</td>
<td>287.764(8)</td>
<td>Bi</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.104(2)</td>
<td>1.5(1)</td>
<td>0.411(4)</td>
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<td></td>
<td>V</td>
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<td>0.348(3)</td>
<td>0.173(3)</td>
<td>0</td>
<td>0.1(1)</td>
<td>1</td>
<td></td>
<td></td>
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<tr>
<td></td>
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<td>8h</td>
<td>0.1518(2)</td>
<td>0.1943(1)</td>
<td>0</td>
<td>0.63(3)</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>8h</td>
<td>0.5404(1)</td>
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<td>0</td>
<td>0.63(3)</td>
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<td>67.5 K, ( I4/m ), ( R_{wp} = 4.720% )</td>
<td>Metallic phase (34%)</td>
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<td>9.9194(2)</td>
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<td>0.168(7)</td>
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<tr>
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<td>10 K, ( I4/m ), ( R_{wp} = 5.521% )</td>
<td>Insulating phase (66%)</td>
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<td>9.8978(1)</td>
<td>2.94526(6)</td>
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<td>0.1930(2)</td>
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<tr>
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<tr>
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<td>8h</td>
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3.2 Magnetization

We first present the magnetization data for a powder sample of Bi\(_{1.7}\)V\(_8\)O\(_{16}\). Unlike the hollandites K\(_2\)V\(_8\)O\(_{16}\) and Rb\(_2\)V\(_8\)O\(_{16}\),\(^{28,30}\) the magnetic susceptibility of Bi\(_{1.7}\)V\(_8\)O\(_{16}\) increases sharply at the transition temperature (\( T_{MIT} \)) upon cooling (Fig. 5a), with two steps of increasing susceptibility observed, indicative of non-spin-singlet formation in the insulating phase. Furthermore, hysteretic behavior is observed in the magnetic susceptibility with the ZFC (measured upon heating) having a slightly higher \( T_{MIT} \) than the FC curve (measured upon cooling). This is consistent with the NPD data showing a large amount of phase coexistence during the first-order phase transition.

Interestingly, the susceptibility of the high-\( T \) metallic phase does not appear to be temperature independent as would be expected for a metallic Pauli paramagnet. Instead, the broad maximum near 275 K is indicative of low-dimensional magnetism associated with local moments in a 1D chain, for example. Earlier studies of Bi\(_{1.7}\)V\(_8\)O\(_{16}\) showed similar broad features in the metallic state,\(^{23,31,32}\) whereas the \( T_{MIT} \) and extent of the susceptibility's divergence were dependent on the Bi\(^{3+} \) content and thus the charge of the V cations. This result indicates that while most electrons near the Fermi level are delocalized, some localized
behavior arises possibly due to significant electron correlations even in the metallic state.

Despite the divergence of the magnetization below the MIT, Bi$_{1.7}$V$_8$O$_{16}$ never enters a ferromagnetic state. While it appears it could be diverging much in the same way as an antiferromagnet above the Neél temperature, the magnetization never drops even at the lowest temperature of our SQUID measurement (2 K). Finally, measuring the magnetization as a function of magnetic field revealed no long range magnetic order (Fig. 6), as the magnetization varied linearly as a function of $H$, similar to either paramagnetic or antiferromagnetic behavior. While the $M$ vs. $H$ curve is neither proof for or against long-range antiferromagnetic ordering, in the context of other results such as neutron diffraction, Bi$_{1.7}$V$_8$O$_{16}$ does not appear to develop long-range magnetic order below the MIT.
3.3 Magnetotransport

First, electrical transport measurements were carried out on polycrystalline material. The resistivity data for a sintered pellet of Bi$_{1.7}$V$_8$O$_{16}$ is presented in Fig. 5b, where a transition from a metallic to an insulating state occurs close to 70 K, concomitant with the observed magnetic transition. The resistivity is 7 orders of magnitude larger near 40 K than at 300 K, confirming the true MIT nature of the transition.

To better understand how crystallographic direction influences the transport properties and the effects of an external magnetic field, single crystals were measured in the PPMS. The transport measurements of a single crystal of Bi$_{1.7}$V$_8$O$_{16}$ as a function of temperature, magnetic field strength, and crystallographic direction are all presented in Fig. 7. The crystals were needle-like in morphology due to the hollandite’s quasi-1D structure, and field was applied either parallel or perpendicular to the needle axis, which corresponds to the c-axis.

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The electrical resistivity data shown in Fig. 7 demonstrates that field applied normal to the ladder direction suppresses the MIT. Upon cooling, the zero field data shows an MIT close to 62.5 K, where resistivity increases over six orders of magnitude compared to that of room temperature; upon heating, the crystal re-enters the metallic state but at a higher temperature of 80 K, demonstrating a first-order MIT with large hysteresis. Fig. 8a shows an overall linear trend for the transition temperature $T_{\text{MI}}$ plotted versus $H_{\parallel}$, where hysteretic behavior appears to widen as $H_{\parallel}$ approaches 8 T.

When field is applied along the needle direction, and therefore along the triangular ladder, $T_{\text{MI}}$ appears to be independent of field strength. The MIT is suppressed to approximately 40 K upon cooling and approximately 65 K upon heating regardless of $H$ (Fig. 8b). This likely indicates that the external field suppresses formation of the V–V dimers, and the effect is more extreme when it is directly along the bond-axis.

The metal–insulator transitions have a much more sudden onset for $H_{\parallel}$ than for $H_{\perp}$, where the resistivity upon cooling suddenly diverged around 35–40 K, beyond the detection threshold of the instrument, as seen in Fig. 7b. These directional experiments thus demonstrate that the coupling between the V cations must be anisotropic, with exchange interactions both along the ladder and its rungs driving the MIT.

3.4 Single crystal diffraction

To understand the behavior of the insulating phase as observed in the magnetization and magnetotransport data, we performed multiple diffraction studies of single crystal and polycrystalline Bi$_{1.7}$V$_8$O$_{16}$ at various temperatures. Full structures were obtained at 90 K, 200 K, and 300 K, while shorter measurements were carried out between 90 K to 300 K in 20 K steps to follow the thermal expansion. The lattice parameters as a function of temperature are presented in Fig. 4, and no phase transition is observed in this

![Fig. 8](image_url) The linear dependence of the transition temperature $T_{\text{MI}}$ vs. applied magnetic field for (a) $H_{\perp}$ and (b) $H_{\parallel}$. Filled symbols indicate $T_{\text{MI}}$ as sample was heated, open symbols are for $T_{\text{MI}}$ upon cooling.

![Fig. 9](image_url) (a) Single crystal XRD data obtained at 90 K showing the main ($h0l$) reflections (white circles) and the satellite reflections corresponding to the Bi charge density wave, which can be indexed with a modulation vector of 0.154c*. (b) The (0kl) reflections of the Bi$_{1.7}$V$_8$O$_{16}$ single crystal X-ray diffraction measurement, also showing the satellite reflections indicative of long-range modulation of the Bi cations within the hollandite channels. Faint streaking between satellite peaks indicates disorder amongst neighboring channels. No satellite reflections or streaking are observed in (c), showing the (hk0) reflections.
temperature regime. Structural and lattice parameters at 200 K can be found in Table 2, and crystallographic information files for the full 200 K and 300 K structures can be found in ESI.†

From the single crystal results, Bi$_{1.7}$V$_8$O$_{16}$ adopts a body-centered tetragonal space group I4/m with the $a$-parameter determined by the size of the hollandite walls and the $c$-parameter by the V-V distances down the triangular ladder. At 200 K, the V-V distance in the $c$-direction is 2.913(1) Å and 2.999(1) Å along the ladder rungs (Fig. 1a).

Remarkably, overlapped frames of the reciprocal lattice map of the ($h0l$) and (0kl) planes of Bi$_{1.7}$V$_8$O$_{16}$ reveal satellite reflections as intense as the main reflections (Fig. 9a and b), indicating the presence of a charge density wave (CDW). Up to fourth order reflections can be observed for the CDW satellites. Interestingly, the CDW in Bi$_{1.7}$V$_8$O$_{16}$ is quasi-commensurate with the VO$_6$ framework as evidenced by the satellite reflections located close to (0 0 0.846e*) or similarly (0 0 −0.154e*). We observed the CDW at all temperatures for the single crystal data within 90 K and 300 K. Since we did not observe a temperature dependence in the location of the satellite reflections, the CDW is not truly incommensurate or independent from the VO$_6$ framework. Rather, it is commensurate with a very long unit cell of $a \times a \times 13c$. Hence, we refer to this as a quasi-commensurate CDW. Furthermore, no satellite reflections were observed in the (hh0) reflections (Fig. 9c) indicating that the CDW only occurs in the $c$-direction. Due to electrostatic repulsion between the cations in the hollandite channels, the Bi$^{3+}$ cations deviate away from their average crystallographic position to form the CDW, a well known phenomenon in Ti-based hollandites.33,34

4 Discussion

In light of the structural and transport data, we would like to discuss the implications for charge, spin, and orbital order in Bi$_{1.7}$V$_8$O$_{16}$.

4.1 Charge order

Studies of the MITs in hollandites have revealed charge order as one of the prerequisites for such behavior. K$_2$V$_8$O$_{16}$ undergoes a two-step MIT between 155–170 K, with an accompanying decrease in magnetization.30 Through high-resolution diffraction studies Komarek et al. observed a structural transition from tetragonal to monoclinic in K$_2$V$_8$O$_{16}$ and proposed a complex CDW formation down the triangular ladders of the hollandite.22 In their model, Komarek et al. find that entire ladders are composed of either V$^{3+}$ or V$^{4+}$. Similarly, the Pb$_{1.7}$V$_8$O$_{16}$ hollandite undergoes a MIT at 140 K; however, initial studies have yet to resolve whether charge ordering or significant structural transitions occur in this system.35

Previous studies on structurally related hollandites that do not undergo MITs, however, could be revealing in formulating the correct model for CDWs in hollandite oxides.33,34,36 The work of Carter and Withers on titanium-based hollandites have shown a correlation between the wavelength of the CDW’s modulation and the occupancy $x$ in A$_2$Ti$_4$O$_{16}$ where A is typically a large cation such as Ba$^{2+}$ or K$.33,34,36$ Carter and Withers connected the modulation of the propagation vector to the occupancy of the A cation through the relationship $x = 2(1 − (1/m))$ where $m$ is the ratio between the repeat period of the CDW.34 For the title compound Bi$_{1.7}$V$_8$O$_{16}$ since the propagation vector of the CDW is 0.846e* (Fig. 9a and b), $m = 0.154$ from the Carter–Withers expression. This ‘compositional ruler’ from the CDW would lead to an $x = 1.69$, consistent with the nominal and refined values of the Bi stoichiometry from NPD and X-ray diffraction data. Since 0.154 is very close to 2/13, this would physically correspond to two Bi vacancies occurring across every 13 unit cells along the channel direction.

Our single crystal diffraction data suggests a charge ordering model for Bi$_{1.7}$V$_8$O$_{16}$ different from that of the other vanadium hollandites such as K$_2$V$_8$O$_{16}$ and Rb$_2$V$_8$O$_{16}$. The average oxidation state of vanadium in Bi$_{1.7}$V$_8$O$_{16}$ is V$^{3.66}$, which would imply five V$^{3+}$ (S = 1) for every three V$^{4+}$ (S = 1/2) cations in the triangular ladder. The absence of a Bi$^{3+}$ cation in the tunnel would require nearby V cations to be in the higher oxidation state of 4+ in order to maintain charge balance. Therefore, the V$^{4+}$ cations would order around the 2/13 Bi vacancies in the CDW to charge compensate the lattice. A schematic of the proposed charge ordering is depicted in Fig. 10a. Kanke et al. propose a similar CDW for the tunnel cations in the Ba$_{1.09}$V$_8$O$_{16}$ hollandite,32 and Kuwabara et al. a similar CDW for the transition metals in the hollandite K$_{1.6}$Mn$_8$O$_{16}$.38 Interestingly, Mentre` et al. found that having $x < 1.7$ for the Bi site or mixing it with a variety of cations leads to A-site disorder and the compounds become semi-conducting at all temperatures.39 Therefore, the CDW seems to be key for the observation of the MIT.

Careful inspection of the ($h0l$) and (0kl) maps in Fig. 9a and b, respectively, reveal another interesting feature with respect to the CDW. Although the satellite reflections at ±0.846e* are fairly strong, there is some streaking which occur in the $h$- and $k$-directions. These arise from a finite amount of disorder between neighboring CDWs in the hollandite’s tunnels. Indeed, Carter and Withers found that quenching titanate hollandites can lead to complete disorder of the CDWs and the reflections become lines in the electron diffraction patterns.34 Their XRD powder patterns

![Diagram](image-url)
nicely demonstrate that the satellite reflections are much stronger when the hollandites are slow cooled. Likewise in our case, we found that the polycrystalline samples of Bi$_{1.7}$V$_8$O$_{16}$ display some evidence for the CDW in the synchrotron data (Fig. S1 in ESI†), but the satellite peaks are particularly weak due to the disorder of the CDW. Interestingly, the satellite of the (002) reflection seemed the broadest on account of the disorder along the c-direction. The multigram polycrystalline sample of Bi$_{1.7}$V$_8$O$_{16}$ utilized for neutron powder diffraction did not display the CDW satellite reflections due to the large amount of disorder between the CDWs that cause a smearing of the reflections. This causes the reflections to appear as background, not as well-resolved Bragg reflections. For the single crystal X-ray diffraction measurements, the samples of Bi$_{1.7}$V$_8$O$_{16}$ were grown through slow cooling in a salt flux, as described previously, and therefore the CDW manifests as well-localized Bragg reflections with some delocalization normal to the [001] direction (Fig. 9).

### 4.2 Orbital order

Next, we address orbital ordering. Due to the octahedral coordination of the vanadium cations, we anticipate the normal ‘3 below 2’ crystal field splitting of the d-orbitals. Since the V cations reside on the 8h Wyckoff position in space group I4/m (Table 1), the local symmetry is actually lower than Oh, and only contains a mirror plane with four unique V–O bond distances ranging from 1.844 Å to 2.021 Å at 200 K. Therefore, we can only approximate the crystal field as octahedral. Within this scheme, the e$_g$ orbitals are aligned along the V–O bonds while the t$_{2g}$ orbitals are involved in coupling the V cations to one another in the triangular ladder. In the charge ordered state, all the V cations should be orbitally active since they are in either the t$_{2g}$ or e$_g$ state.

In the present system, we illustrate the orientation of the various t$_{2g}$ orbitals within the hollandite-type structure of the present compound. The d$_{xy}$ orbital is oriented such that one pair of lobes is parallel to the tunnel direction. The four-fold crystal symmetry renders the d$_{xz}$ and d$_{yz}$ orbitals equivalent, pointing along the triangular ladder rung direction as shown in Fig. 10b.

Orbital ordering is supported by the first-order structural distortion observed in the NPD data, where a large phase coexistence was observed between the insulating and metallic phases. Coupling of dimers along the tunnel direction would cause an increase in overlap between paired d$_{xy}$ orbitals, further lifting the three-fold degeneracy of the t$_{2g}$ orbitals. With an approximate ratio of five V$^{3+}$ to three V$^{4+}$ cations, the majority of dimers would then be either V$^{3+}$–V$^{3+}$ pairs, or V$^{3+}$–V$^{4+}$ pairs.

The theoretical work on Bi$_{1.7}$V$_8$O$_{16}$ of Shibata et al. suggests that orbital ordering is required to observe the MIT. By deriving a spin–orbit Hamiltonian by second-order perturbation theory, Shibata et al. find a variety of orbitally ordered phases and suggests that each one contains a different ground spin state. Interestingly, one of these phases contains a majority of spin-singlets interspersed with unpaired $S = 1/2$ minority states. This could explain the results from the solid state NMR studies of Bi$_{1.7}$V$_8$O$_{16}$ by Waki et al. A charge ordered state is proposed by Waki et al. along with orbital ordering leading to spin singlet formation and finally to long-range antiferromagnetic ordering near 20 K. We partially agree with some of the conclusions of Waki et al. in that spin singlet formation comprises the majority of the states in Bi$_{1.7}$V$_8$O$_{16}$. Our NPD data, however, conclusively demonstrate no such long-range antiferromagnetic phase sets in below 20 K.

The recent computational studies from Kim et al. suggest that spin, orbital, and lattice degrees of freedom are all coupled in the related K$_2$V$_8$O$_{16}$ hollandite. The orbital ordering manifests in a Jahn–Teller type fashion, but Kim et al. suggest that Mott-type physics rather than Peierls-type mechanism predominates with the electronic bands from the d$_{xy}$ orbital playing the decisive role.

Orbital physics seems to be quite generally in hollandites, and goes beyond the vanadates. In the structurally related system K$_2$Cr$_8$O$_{16}$ long-range ferromagnetic ordering sets in below 180 K. For this system, the interaction between the charge and orbitally ordered Cr$^{3+}$ and Cr$^{4+}$ cations seems key to the formation of such an unusual ground state—a ferromagnetic insulator. The theoretical work by Mahadevan et al. showed that ordering of the t$_{2g}$ orbitals, which are the most significant for the M–M interactions in hollandites, would lead to ferromagnetic coupling between the cations.

### 4.3 Spin order

Finally, we address spin ordering in Bi$_{1.7}$V$_8$O$_{16}$. As shown in Fig. 10b, we label the magnetic exchange along the ladder direction as $J_1$ and that along the rungs as $J_2$. It appears that the majority of the magnetic exchange interactions are antiferromagnetic in nature as evidenced by the magnetization data in the high-$T$ phase. Above the MIT the magnetization data (Fig. 5) reveals a broad feature that appears similar to the Bonner–Fisher susceptibility for Heisenberg chains with a negative $J$. For Bi$_{1.7}$V$_8$O$_{16}$, the chains consists of predominantly $S = 1$ cations, and therefore the Bonner–Fisher relation becomes $kT_{\text{max}}/|J| = 2.70$ where $k$ is the Boltzmann constant and $T_{\text{max}}$ is where the susceptibility is at a maximum. For the FC data (Fig. 5) $T_{\text{max}}$ is approximately 275 K. This value is quite high, and for one-dimensional materials this causes the susceptibility to broaden out in temperature. Based on this relation, we can estimate the exchange interaction $J_1$ to be close to 8.31 meV.

At the MIT, the system appears to go from a quasi-1D chain of antiferromagnetically coupled V cations to a dimerization of V–V pairs. Therefore, the system goes from an extended solid of $N$ centers to one that could be modeled as akin to N/2 molecules where $N$ is Avogadro’s number. Although the majority of Js remain negative, it does appear that some of the V–V ‘molecules’ are ferromagnetically coupled.

Consider the Hamiltonian for a system consisting of dimers with the interatomic axis being the z-axis as given by

$$\mathcal{H} = g_{\text{I}} S_1 S_2 H_z - 2 J S_1' S_2'$$

(1)

where $S_1$ and $S_2$ would correspond to the spins of the two nearest neighbors in the V–V dimers, $S_1'$ is the operator for the z-component of the total spin of the dimer, $H_z$ is the external field applied along the z-axis, and $g$ the Landé factor. For two
interacting spin-1/2 electrons, eqn (1) leads to the so-called Bleaney–Bowers equation for susceptibility given by

\[ \chi = \frac{2N \mu_B^2}{kT(3 + e^{kT/\mu})} \]

(2)

where \( \Delta \) is the energy gap between the two quantum numbers that describe the spin states of the dimer. For a positive value for \( J \) in eqn (1), the ground state of the system would be \( S = 1 \) (i.e. triplet state) and the excited state \( S = 0 \) (i.e. singlet state), with an energy gap of \( \Delta \) between the states. While eqn (2) does not necessarily apply to our dimers of \( \text{V}^{3+} \) and \( \text{V}^{4+} \) cations since they are of mixed spin states, the expression is informative in qualitatively describing the magnetization data below the MIT.

For ferromagnetic coupling between the vanadium cations, a negative value of \( \Delta \) (positive \( J \)) is found and therefore the susceptibility of eqn (2) is seen to diverge at lower temperatures. For antiferromagnetic coupling, this susceptibility decreases to zero as \( 0 \) \( K \) is approached. Unlike all other vanadates undergoing an MIT, \( \text{Bi}_{1.7} \text{V}_{8} \text{O}_{16} \) clearly shows the former. Fig. S2 in the ESI† compares the Bleaney–Bowers model for ferromagnetic and antiferromagnetic coupling between two \( S = 1/2 \) cations.

While this model cannot be used to fit the magnetic susceptibility data, Fig. S2 (ESI†) does allow the reader to qualitatively compare the two models against the low temperature susceptibility of \( \text{Bi}_{1.7} \text{V}_{8} \text{O}_{16} \) below the MIT.

In the case of \( \text{Bi}_{1.7} \text{V}_{8} \text{O}_{16} \), multiple steps are clearly seen in the ZFC and FC curves, below the MIT indicating the formation of ferromagnetically coupled dimers (Fig. 5a). The hysteresis in the ZFC/FC curves should also rule out the possibility that these are just isolated ions producing a Curie tail. Furthermore, the magnetotransport data clearly indicate that the magnetic field controls the extent of the MIT and therefore enters into the coupling energy between the \( \text{V} \)–\( \text{V} \) centers (eqn (1)).

Even though both antiferromagnetic and ferromagnetic coupling is observed between the \( \text{V} \)–\( \text{V} \) dimers, the NPD data clearly indicate that no long-range ferromagnetic or antiferromagnetic ordering occurs. This suggests that the nature of magnetic interactions are either 1D or nearly 1D so that no magnetic Bragg reflections of long-range ordering ever occur. The triangular nature of the ladders likely also contribute to a frustration that disallows long-range ordering.

5 Conclusions

We have described a metal–insulator transition for a quasi-one dimensional system containing a mix of \( S = 1 \) and \( S = 1/2 \) vanadium cations. Unlike all other known vanadates, the magnetic susceptibility of \( \text{Bi}_{1.7} \text{V}_{8} \text{O}_{16} \) diverges below \( T_{\text{MIT}} \), although no long-range magnetic ordering is observed from neutron diffraction. The magnetotransport measurements reveal that the transition temperature is suppressed upon application of an external magnetic field, and this behavior is both hysteretic and anisotropic. A first-order structural transition is revealed by the coexistence of two tetragonal phases near the MIT indicative of dimerization between the mixed-spin cations. The MIT is thus best understood in terms of the interplay between the charge and orbital ordering of the V cations along the triangular ladder directions.

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