

## Supporting Information

### Exotic Magnetic Properties in Zintl Phase BaVSe<sub>3</sub>: A Theoretically Supported Experimental Investigation

Chinnu V. Devan<sup>1,2</sup>, Anoop A. Nair<sup>3</sup>, Ramany Revathy<sup>4,5</sup>, Biswapriya Deb<sup>1,2,\*</sup>,

Manoj Raama Varma<sup>2,4,\*</sup>

<sup>1</sup>*Photosciences and Photonics, Chemical science and Technology Division, CSIR- National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram- 695019, Kerala, India*

<sup>2</sup>*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India*

<sup>3</sup>*School of Physics (SoP), Indian Institute of Science Education and Research, Thiruvananthapuram- 695551, Kerala, India*

<sup>4</sup>*Materials Science and Technology Division, CSIR- National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram- 695019, Kerala, India*

<sup>5</sup>*Department of Physics, St. John's College, Anchal, Kollam, Kerala, India*

Email: [manoj@niist.res.in](mailto:manoj@niist.res.in), [biswapriya.deb@niist.res.in](mailto:biswapriya.deb@niist.res.in)

**Figure S1:** The constrained geometry optimization reduces the internal forces.

**Figure S2:** Indexed XRD pattern of BaVSe<sub>3</sub> (black color) and BaSe<sub>3</sub> (red color)

**Figure S3:** M versus T, ZFC and FC at **(a)**100Oe **(b)**500Oe

**Figure S4:** The spin-polarized band structure of BaVSe<sub>3</sub>.

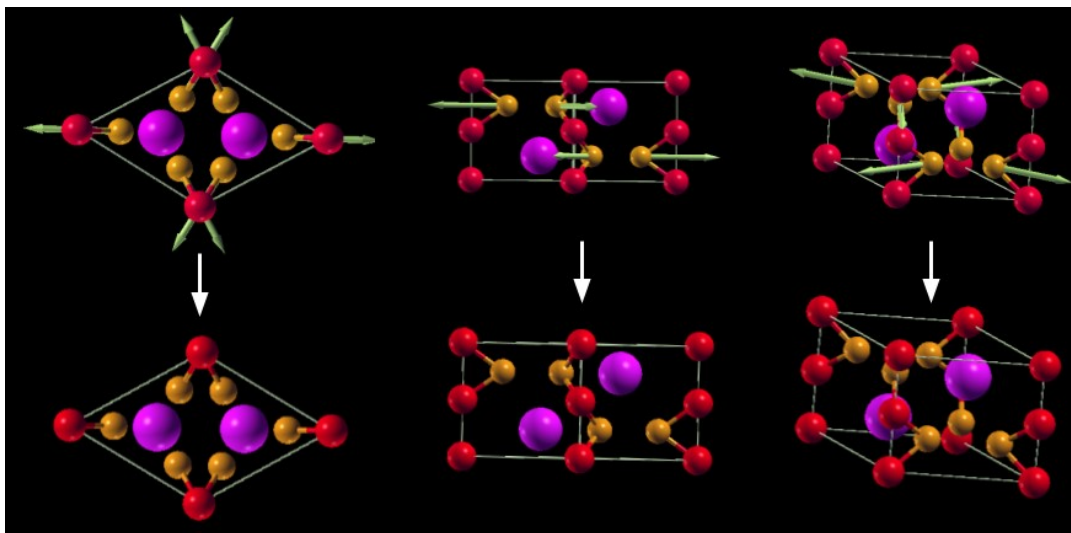
**Figure S5:** The (a) spin-up band structure and (b) spin-down band structure of BaVSe<sub>3</sub>.

**Figure S6:** CW plot at 10000Oe

**Table S1:** The unit-cell lengths and angles of hexagonal BaVSe<sub>3</sub>

**Table S2:** The Wyckoff symbols and the coordinates of Barium, Selenium and Vanadium

## S1. Geometry optimization



**Figure S1:** The constrained geometry optimization reduces the internal forces. The green arrows indicate the forces. Ba, Se and V are given by purple, orange and red spheres respectively.

The  $\text{BaVSe}_3$  structure was subjected to a constrained geometry relaxation (the constraint was on the unit-cell lengths and angles) using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm as implemented in Quantum ESPRESSO. The forces with a magnitude greater than 0.0005 Ryd/a.u. on the individual atoms were checked using Xcrysden to ensure that relaxation has taken place (as given in Figure S4). The relaxed structure obtained was considered for further studies.

## S2. Crystal Structure

Barium Vanadium Selenide ( $\text{BaVSe}_3$ ) crystallizes in the Hexagonal Bravais lattice, specifically in the  $P 63/m 2/m 2/c$  space group (no 194). The structure in the CIF obtained from XRD analysis is subjected to geometrical optimization via the “relax” calculation as implemented in Quantum ESPRESSO (version 6.6) [detailed in Geometry optimization (Section S1)]. The PWscf output file (.out) is then converted to the ‘.xsf’ format using Xcrysden (version 1.6) and is subsequently converted into a CIF format using VESTA (version 3.5.7). Since VESTA creates CIF files conforming to ‘P1’ symmetry, the underlying symmetry of the unit-cell is observed by using the FINDSYM web app (version 7.1.2). The unit cell parameters, Wyckoff symbols and the fractional coordinates of the atoms are provided in the given tables.

**Table S1**

Cell Parameter	Value
Cell Length A	6.9943985000 Å
Cell Length B	6.9943985000 Å
Cell Length C	5.8576980000 Å
Cell Angle Alpha	90.0 <sup>0</sup>
Cell Angle Beta	90.0 <sup>0</sup>
Cell Angle Gamma	120.0 <sup>0</sup>

**Table S2**

Atoms	Wyckoff symbols	x coordinate	y coordinate	z coordinate
Ba	2c	0.33333	0.66667	0.25
Se	6h	0.83195	0.66390	0.25000
V	2a	0	0	0

### S3. CIF to QE Input

The Crystallographic Information File (CIF) was converted to the Quantum ESPRESSO (QE) input file using the cif2cell python module (version 2.0.0 a3). The code creates the QE input file by parsing the CIF file and is executed by the command given below:

```
cif2cell {CIF_file_name}.cif -p quantum-esspresso -o {Input_file_name}.in
```

Here the “CIF\_file\_name” and “Input\_file\_name” should be the name of the concerned CIF and input files respectively. Convergence tests were done to obtain the optimum K-point grid, plane wave cutoffs and charge density cutoffs of 8x8x8, 80 and 640 respectively.

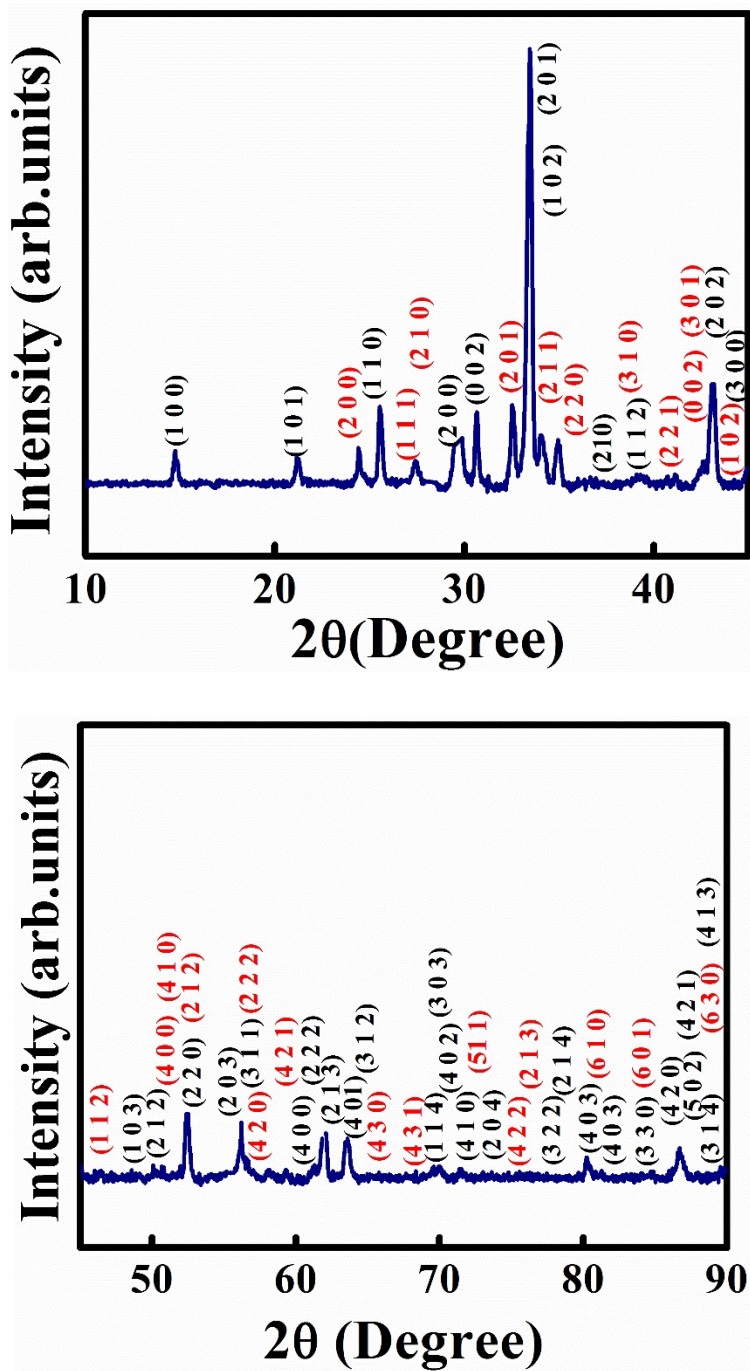
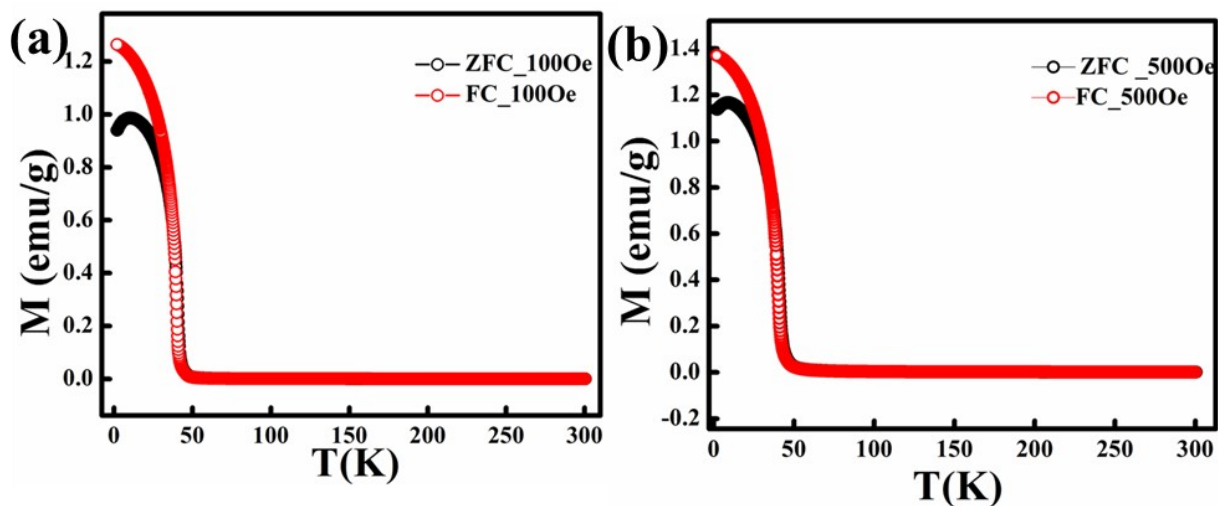


Figure S2. Indexed XRD pattern of  $\text{BaVSe}_3$  (black color) and  $\text{BaSe}_3$  (red color)

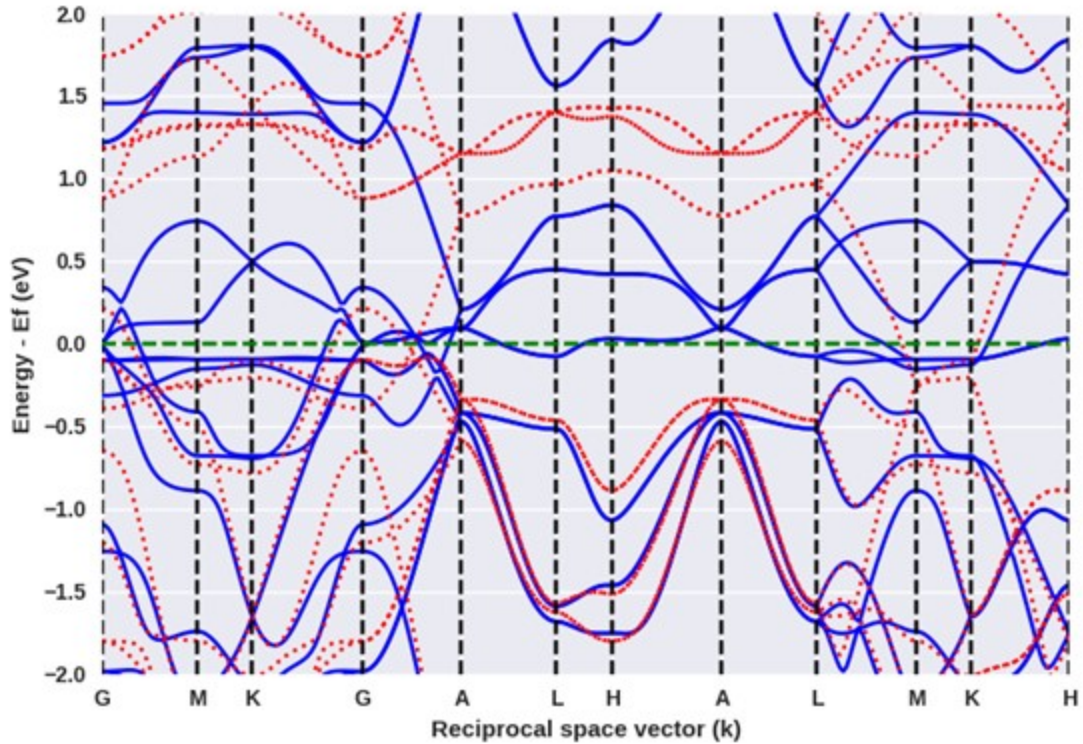


**Figure S3.** M versus T, ZFC and FC at (a)100Oe (b)500Oe

## S4. Electronic structure calculation

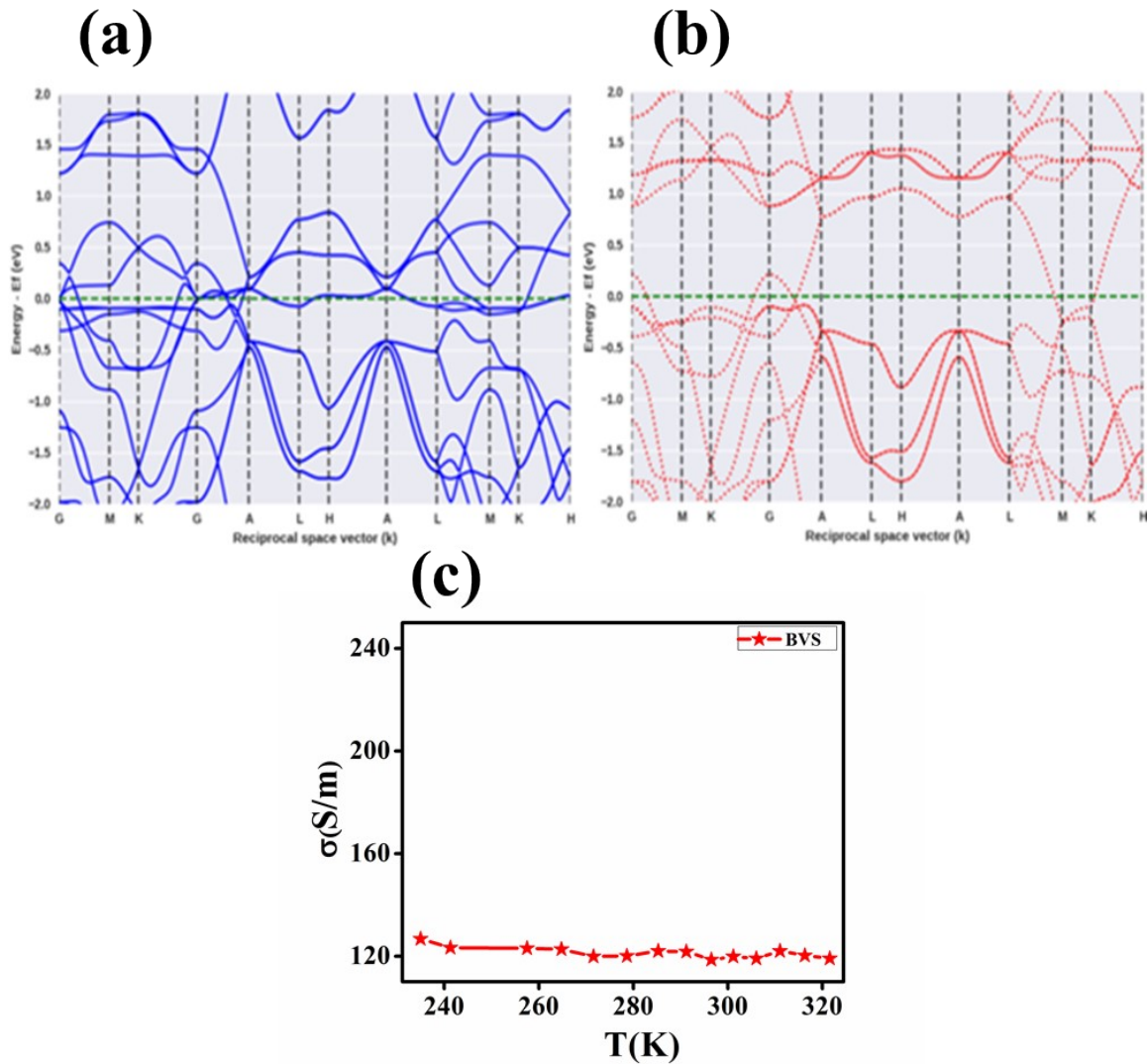
### S4.1. Band Structure

The electronic behavior of the material can be understood via the analysis of the ground-state electronic structure. The band structure calculation involved a Self-Consistent Field (SCF) calculation over a k-point grid of  $8 \times 8 \times 8$  and a non-self-consistent field (NSCF) calculation on a  $16 \times 16 \times 16$  dense k-point grid with 170 bands taken into consideration along with the ‘tetrahedra’ occupations. This was followed by the calculation of energy eigen values along a path connecting the high symmetry points in the Brillouin Zone for the hexagonal unit. The k points were taken along the path "G-M-K-G-A-L-H-A|L-M|K-H " through the Brillouin zone with a spacing of 30 points between each pair of high symmetry points. The spin-polarized band (given in Figure S4) structure correctly predicts the material to be metallic in nature.



**Figure S4.** The spin-polarized band structure of BaVSe<sub>3</sub>. The blue and red bands indicate the spin up and down channels respectively. The fermi-level is given by the green dashed line at 0.

From Figure S5 (a), it is observed that the spin-up channel dominates at the Fermi-level and the bands are almost dispersion-less and flat. The spin-down channels (Figure S5 (b)) are much more curved and crosses the Fermi-level at the M, K and Gamma (G) high symmetry points.



.Figure

e S5. The (a) spin-up band structure and (b) spin-down band structure of BaVSe<sub>3</sub> (c) experimentally obtained conductivity versus temperature plot

#### S4.2. The density of states (DOS) calculation

The Self-Consistent Field (SCF) calculation, which was done on a k-point grid of 8x8x8, was followed by a non-self-consistent field (NSCF) calculation with a dense k-point grid of 16x16x16. This was done with the number of bands taken as 170 respectively. The DOS calculation was then executed via the **dos.x** module of Quantum ESPRESSO.

#### S4.3. Magnetic moments

A spin polarized charge density calculation is carried out using the post-processing module (**pp.x**) module of Quantum ESPRESSO.

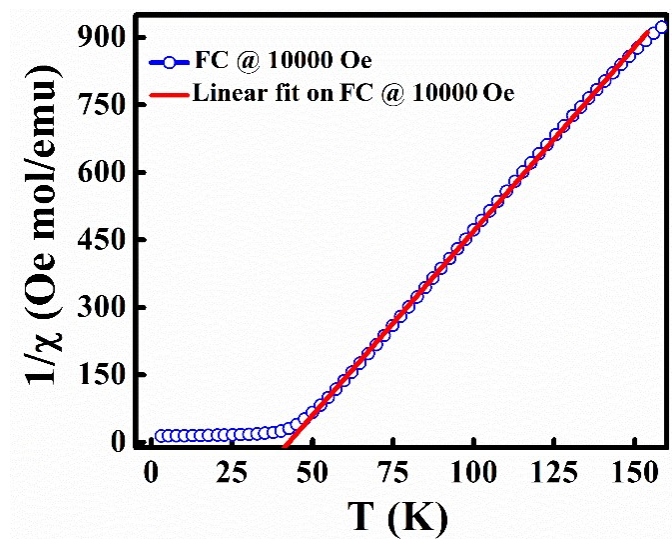


Figure S6. CW plot at 10000Oe