

**Supplementary Information: Pressure-induced 1T to 3R
structural phase transition in metallic VSe₂: X-ray diffraction and
first-principles theory**

Srishti Pal,^{1,*} Koyendril Debnath,^{2,*} Satyendra Nath Gupta,¹ Luminita
Harnagea,³ D. V. S. Muthu,¹ Umesh V. Waghmare,² and A. K. Sood^{1,†}

¹*Department of Physics, Indian Institute of Science, Bengaluru 560012, India*

²*Theoretical Sciences Unit, Jawaharlal Nehru Centre for
Advanced Scientific Research, Bengaluru 560064, India*

³*Department of Physics, Indian Institute of Science
Education and Research, Pune 411008, India*

I. REPRODUCIBILITY OF XRD DATA

Figure S1 shows the angle dispersive XRD patterns of VSe_2 for another run with the same wavelength of 0.4957 \AA . New reflections start appearing around 11.6 GPa at same Bragg angles as that for the pressure run shown in the main text (Fig. 2). This pressure run was not used for analysis due to higher noise level and incompleteness of the run due to technical difficulties.

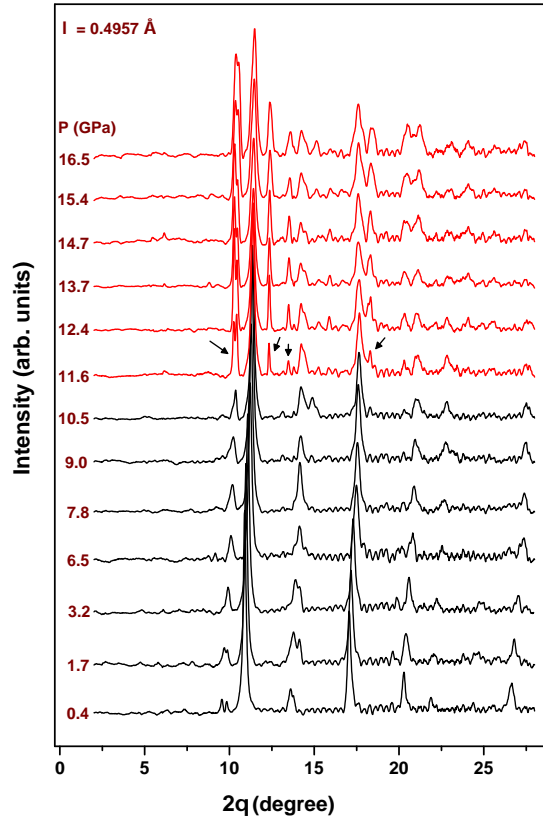


FIG. S1: Stacked XRD patterns VSe_2 with increasing pressures from 0.4 to 16.5 GPa. Arrows indicate new peaks appearing at the onset of the 1T to 3R transition.

II. RIETVELD FITS WITH MONOCLINIC STRUCTURES

Figure S2(a) shows the superposition of the XRD data taken from Ref. 1 and our 12.2 GPa PXRD pattern (transformed according to the wavelength 0.4133 Å used in Ref. 1). Our high-pressure XRD pattern with several new intense Bragg reflections (at $\sim 10.3^\circ$, 12.3° , 13.5° , 15.9° , 18.3° , 20.3° , 22.1° , and 23.8°) is in disagreement with what reported in Ref. 1. Fig. S2(b)-(d) shows the best possible Rietveld refined fitted patterns at 12.2 GPa using three monoclinic superstructures reported by Sereika et al.¹ The fitted lattice parameters are given in Table SI. As seen from the fits, none of the three monoclinic structures could fit the high-pressure structure.

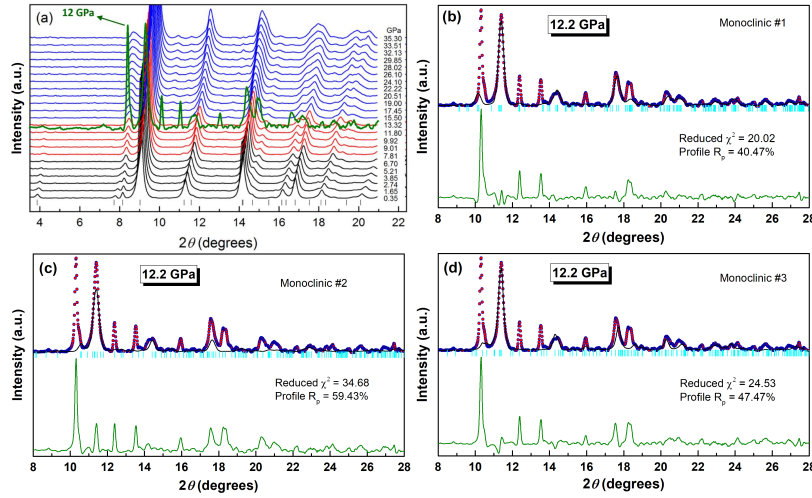


FIG. S2: (a) Black, red, and blue curves are the XRD patterns of VSe₂ taken from Ref. 1. Green curve denotes the XRD pattern at 12.2 GPa as obtained from our PXRD experiments. (b), (c), and (d) Rietveld refined XRD patterns of VSe₂ at 12.2 GPa using the monoclinic $C2/m$ structures #1, #2, and #3, respectively taken from Ref. [1]. Solid circles, black solid lines, dark green curves, and cyan vertical bars represent the experimental data, calculated patterns, weighted difference between observed and calculated profiles, and reflection positions, respectively.

TABLE SI: Best fitted lattice parameters at 12.2 GPa using monoclinic structures of Ref. [1].

Monoclinic ($C2/m$)	a (Å)	b (Å)	c (Å)	β ($^\circ$)	V (Å ³)
#1	12.521654	3.219836	12.576619	143.3383	302.760
#2	10.450211	3.698385	14.646615	148.9436	292.028
#3	16.453749	3.411010	5.361089	87.0747	300.493

III. RIETVELD FIT AT 12.2 GPa WITH FIXED U -PARAMETERS

Figure S3 shows the refinement of the phase fractions using Rietveld algorithm in the mixed phase of VSe_2 (1T+3R) at 12.2 GPa with U -parameters fixed at values $U_{11}(\text{V}) = U_{33}(\text{V}) = 0.012$ and $U_{11}(\text{Se}) = U_{33}(\text{Se}) = 0.02$ similar to those at the low pressure 1T phase to have a smooth variation across the 11 GPa structural transition. It is clear from the figure that refinement of the phase fraction alone cannot account for accurate relative intensities for the Bragg reflections of the 3R phase. The U -parameters have to be refined along with the phase fraction (as done in Fig. 2 of the main manuscript) to fit the experimental pattern with the calculated one.

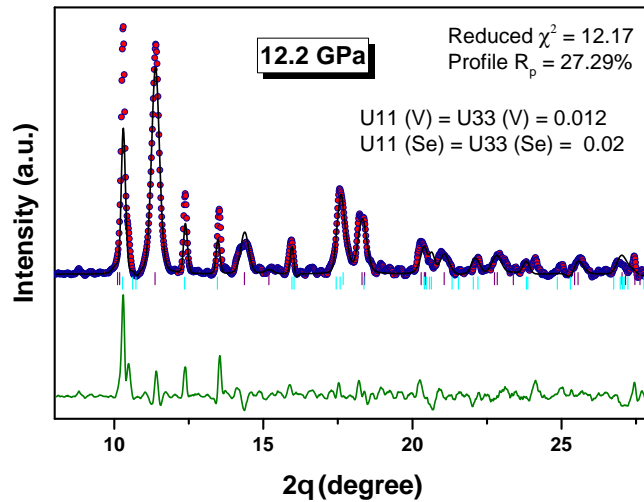


FIG. S3: Rietveld refined XRD pattern of VSe_2 at 12.2 GPa with U -parameters fixed at values $U_{11}(\text{V}) = U_{33}(\text{V}) = 0.012$ and $U_{11}(\text{Se}) = U_{33}(\text{Se}) = 0.02$ (similar to the values for the low pressure 1T phase).

IV. STABILITY ANALYSIS OF $R\bar{3}M$

Figure S4 shows the enthalpy difference between the 3R ($R\bar{3}m$) and 1T ($P\bar{3}m1$) phase $\Delta H = H(R\bar{3}m) - H(P\bar{3}m1)$ using the optimized lattice constants (Table SII) obtained by relaxing the structures in QE. ΔH remains positive for the entire range of pressure failing to stabilize the 3R structure.

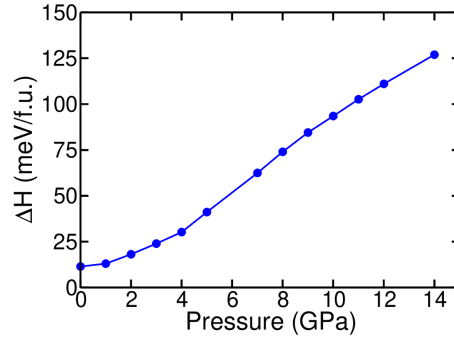


FIG. S4: Variation of difference in enthalpy between 3R ($R\bar{3}m$) and 1T ($P\bar{3}m1$) structures of VSe_2 with pressure.

TABLE SII: Calculated lattice parameters (in \AA) using Quantum ESPRESSO and ABINIT for 1T and 3R structures of VSe_2 at $P = 0$ and 12 GPa compared to experimental values.

1T-VSe_2		a (\AA)	c (\AA)	V (\AA^3)
0 GPa	QE	3.31	6.24	59.33
	ABINIT	3.32	6.27	60.02
0.2 GPa	Exp.	3.35	6.10	59.30
12 GPa	QE	3.21	5.49	48.96
	ABINIT	3.22	5.55	49.69
12.2 GPa	Exp.	3.23	5.63	50.74
3R-VSe_2		a (\AA)	c (\AA)	V (\AA^3)
0 GPa	QE	3.30	19.07	60.04
	ABINIT	3.32	19.07	60.53
12 GPa	QE	3.16	17.39	50.39
	ABINIT	3.18	17.45	50.83
12.2 GPa	Exp.	3.24	16.07	48.85

Table SIII show the optimized lattice parameters of 3R ($R\bar{3}m$) phase at 12 GPa using various van der Waals interactions, London-s6 forces and Hubbard U parameters. The c -parameter of the 3R phase remains overestimated compared to experiment in all cases.

TABLE SIII: Lattice parameters (in Å) of 3R structure of VSe₂ (space group: $R\bar{3}m$) evaluated using different functionals compared to experiments at P = 12 GPa.

Method		a (Å)	c (Å)
van der Waals interaction	Grimme-D2	3.16	17.39
	Df-c09	3.15	17.46
	Df2-b86r	3.17	17.47
London-s6	0.65	3.17	17.41
	0.70	3.17	17.40
	0.75	3.17	17.39
	0.80	3.17	17.38
	0.85	3.17	17.34
	1.50	3.17	17.14
Hubbard-U	1 eV	3.18	17.39
Experiment	-	3.24	16.07

V. STABILITY ANALYSIS OF $2H_a$ AND $R\bar{3}M$

Figure S5 shows the phonon dispersion and enthalpy calculations on the $2H_a$ ($P6_3/mmc$) polytype of VSe_2 using the optimized lattice constants (Table SIV). The phonon dispersion of $2H_a$ at 12 GPa shows its stability with no imaginary modes. The enthalpy difference $\Delta H = H(P6_3/mmc) - H(P\bar{3}m1)$ becomes negative after ~ 12 GPa, theoretically predicting a possible phase transition from 1T to $2H_a$ at ~ 12 GPa.

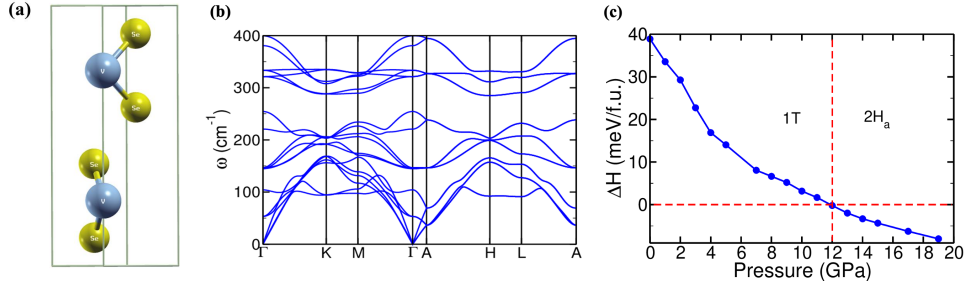


FIG. S5: (a) $2H_a$ crystal structure of VSe_2 , (b) its phonon dispersion at 12 GPa and (c) the difference in enthalpy of $2H_a$ and 1T structures of VSe_2 .

Figure S6 shows the enthalpy calculation based on another 3R structure with $R\bar{3}m$ symmetry (calculated lattice constants are shown in Table SIV). The $R\bar{3}m$ structure only lacks the inversion centred as compared to $R\bar{3}m$ owing to the trigonal prismatic co-ordination of six Se atoms around V (same as $2H_a$). The increasing enthalpy difference $\Delta H = H(R\bar{3}m) - H(P\bar{3}m1)$ does not allow the $R\bar{3}m$ structure to stabilize at higher pressures.

TABLE SIV: Calculated lattice parameters (in Å) for $2H_a$ and 3R structure of VSe_2 (space group:

$R\bar{3}m$) at $P = 12$ GPa.

VSe_2 polytype	a (Å)	c (Å)
$2H_a$	3.20	10.95
3R	3.18	16.91

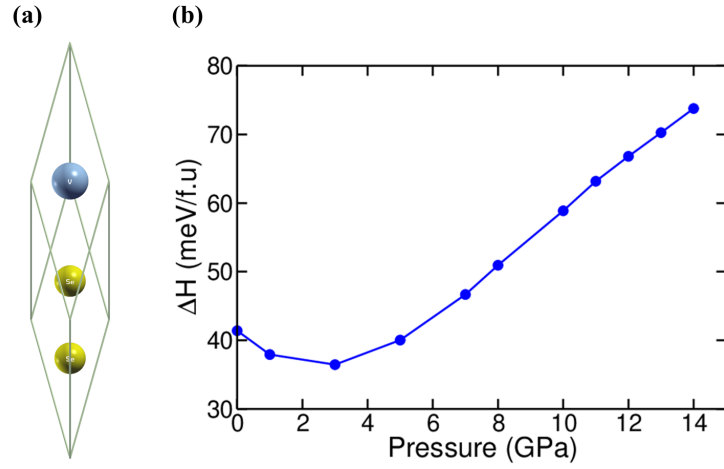


FIG. S6: (a) Rhombohedral primitive cell of 3R ($R\bar{3}m$) VSe₂ and (b) the difference in enthalpy of 3R ($R\bar{3}m$) and 1T structures of VSe₂.

VI. FINITE TEMPERATURE CALCULATIONS ON $R\bar{3}M$ AND $R3M$

The vibrational contributions to the free energies as a function of temperature is estimated within a harmonic approximation:²

$$F_{\text{vib}} = E_{\text{total}} + \frac{k_{\text{B}}T}{N_{\text{q}}} \sum_{q,i} \log \left[2 \sinh \left(\frac{\hbar\omega_{iq}}{2k_{\text{B}}T} \right) \right] \quad (1)$$

where N_{q} is the number of \mathbf{q} -points on a $24 \times 24 \times 12$ mesh in the BZ and ω_{iq} is the frequency of mode i at a wave vector \mathbf{q} . As evident in the transition temperatures at various hydrostatic pressure (Table SV), the temperature that stabilizes 3R polytypes is not realistic (Fig. S7).

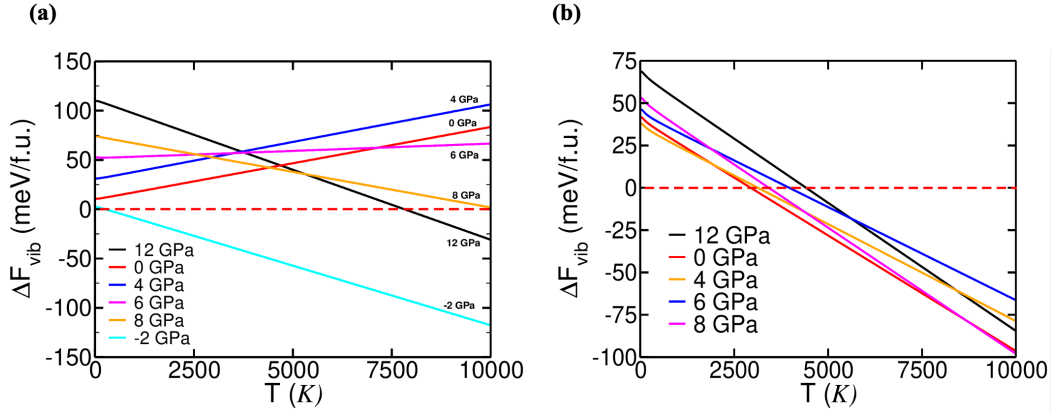


FIG. S7: The difference in vibrational free energy of 3R and 1T structures of VSe_2 as a function of temperature in (a) 3R ($R\bar{3}m$) and (b) 3R ($R3m$).

TABLE SV: Transition temperatures from 1T to 3R structures ($R\bar{3}m$ and $R3m$) at $P = 0, 4, 8$ and 12 GPa.

Pressure (GPa)	T (K)	
	$R\bar{3}m$	$R3m$
0	-	2950
4	-	3140
8	10300	3430
12	7820	4420

VII. STABILITY ANALYSIS OF MONOCLINIC ($C2/m$) SUPERSTRUCTURE

Figure S8 presents our theoretical analysis on the stability of the monoclinic structure $C2/m$ predicted in Ref. [1] using their methodology (projected augmented wave (PAW) method as implemented in Vienna ab-initio simulation package VASP) to obtain the energies (and enthalpies) of 1T and $C2/m$ phases of VSe_2 with the same computational parameters (and the same code). The \mathbf{k} -meshes taken for the 1T and $C2/m$ structures are $8 \times 8 \times 3$, same as those used in Ref. [1]. For the sake of comparison, we have also performed the enthalpy calculation for the 3R phase using a sparse \mathbf{k} -mesh of $8 \times 8 \times 8$. The monoclinic structure (Fig. S8(a)) has lattice parameters $a = 18.68 \text{ \AA}$, $b = 2.76 \text{ \AA}$, $c = 5.63 \text{ \AA}$, $V = 287.41 \text{ \AA}^3$, and $\beta = 97.458^\circ$ at $P = 35 \text{ GPa}$. Fig. S8(b) represents the pressure evolution of enthalpies for the 1T, 3R, and $C2/m$ structures. 3R comes out to be the lowest energy structure at $P = 0 \text{ GPa}$ and a 3R to $C2/m$ transition is indicated at $\sim 3 \text{ GPa}$ (Fig. S8(d)). The pressure evolution of difference in enthalpy of 1T and $C2/m$ shown in Fig. S8(c) (VASP calculation) reveals robust stability of $C2/m$ phase of VSe_2 relative to its 1T structure as a function of pressure. This contradicts the 1T to $C2/m$ phase transition at $P = 15.5 \text{ GPa}$ reported in Ref. [1].

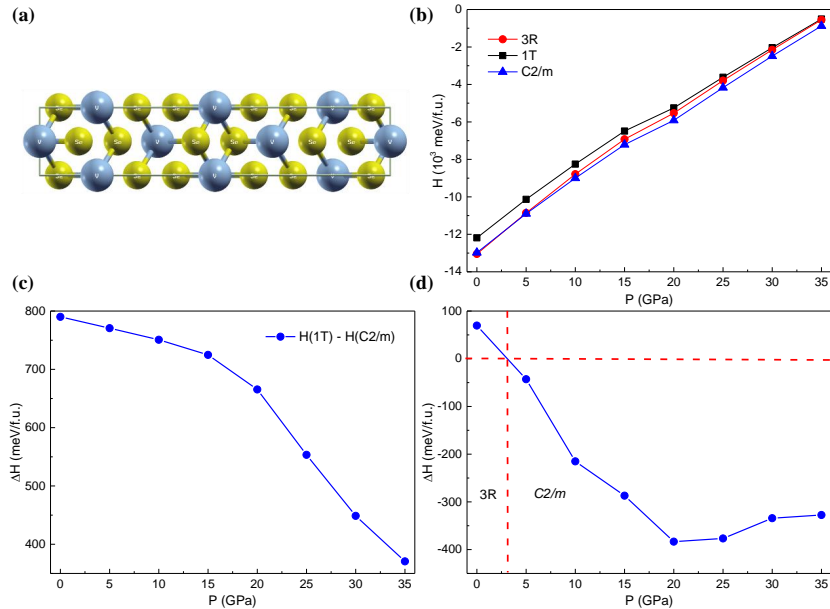


FIG. S8: (a) $C2/m$ structure of VSe_2 and (b) Pressure dependence of enthalpies of the 1T, 3R, and $C2/m$ structures of VSe_2 . (c) and (d) The differences in enthalpies of 1T and $C2/m$, and $C2/m$ and 3R structures of VSe_2 calculated using VASP.

* Both authors contributed equally to this work.

† E-mail: asood@iisc.ac.in

¹ R. Sereika, C. Park, C. Kenney-Benson, S. Bandaru, N. J. English, Q. Yin, H. Lei, N. Chen, C.-J. Sun, S. M. Heald, J. Ren, J. Chang, Y. Ding, and H. kwang Mao, *J. Phys. Chem. Lett.* **11**, 380 (2020).

² A. van de Walle and G. Ceder, *Rev. Mod. Phys.* **74**, 11 (2002).