Dimension-dependent phase transition and magnetic property of VS_2

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Supplementary information

Calculation details

As for the k-points, the 15×15×1, 15×15×4 and 15×15×9 K-meshes were employed for 2D monolayers, bulk 2H-VS_2 and 1T-VS_2, respectively. The phonon property was calculated by using the direct approach implemented in Phonopy package [1, 2]. The Real-space force constants were calculated from the Hellmann-Feynman forces by introducing displacements to supercells based on finite displacement method[3]. Then the dynamical matrices, phonon frequency were obtained via the force constants. In phonon calculations, for 2D monolayers, 4×4 supercells containing 48 atoms were employed and the first BZ was sampled by 6×6×1 K-meshes, while for 3D bulk structures 2H(1T), 2×2×2(4×4×2) supercells containing 48(96) atoms and 6×6×1(2×2×2) K-meshes were used. In order to evaluate the inaccuracy of the calculated transition temperature caused by the different calculation parameters, the free energy uncertainty has to be carefully checked. The phonon calculations of H-VS_2 have been further performed by using 2×2 supercells, 6×6 K-meshes, and 4×4 supercells, 3×3 K-meshes. The free energy change does not exceed 0.3 kJ/mol, in comparison with the given result here with 4×4 supercells, 6×6 K-meshes.

The monolayer VS_2 has two equal lattice constants, $a=b$, and a vacuum layer of at least 10 Å along the c direction. As a result, the structures of monolayer VS_2 were initially fully optimized with atom coordinates relaxed for a series of lattice parameters a. The ground state configuration of VS_2 monolayers was determined by minimizing total energy as a function of lattice parameters. The bulk structures have two identical lattice constants $a=b$ and the third independent c, and consequently they are optimized with both unit cell and atoms coordinates relaxed.

The thermodynamic calculation requires high accuracy of the calculated phonon dispersions. As far as we know, experimental data on phonon dispersions of VS_2 is unavailable to directly verify our calculation. However, the phonon frequencies of MoS_2 have been well determined by both the theoretical and experimental method. As a result, the reliability of phonon calculations is firstly checked by comparing the calculated phonon frequencies of monolayer H-MoS_2 with the previous theoretical and experimental data. The present calculated monolayer phonon frequencies of Raman-active modes, E'=376 cm^{-1}, A_1'=401 cm^{-1}, are comparable with the experimental data characterized by Raman spectroscopy E'=384 cm^{-1}, A_1'=403 cm^{-1} [4, 5]. The results also agree well the other theoretical data, such as E'=376 cm^{-1}, A_1'=401

cm^{-1} by density functional perturbation theory (DFPT) with HGH pseudopotentials and LDA functional, E′=392 cm^{-1}, A_1′=410 cm^{-1}[6] and by DFPT with GGA-PBE, E′=380 cm^{-1}, A_1′=406 cm^{-1} [7]. The small deviation between the current calculated phone frequencies and the available experimental or the previous calculated values confirms the reliability of our calculations.

References

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