Correlating structural, electronic, and magnetic properties of epitaxial VSe2 thin films

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The electronic and magnetic properties of transition metal dichalcogenides are known to be extremely sensitive to their structure. In this paper we study the effect of structure on the electronic and magnetic properties of mono- and bilayer VSe2 films grown using molecular beam epitaxy. VSe2 has recently attracted much attention due to reports of emergent ferromagnetism in the two-dimensional (2D) limit. To understand this compound, high-quality 1T and distorted 1T films were grown at temperatures of 200 °C and 450 °C, respectively, and studied using 4 K scanning tunneling microscopy and spectroscopy. The measured density of states and the charge density wave (CDW) patterns were compared to band structure and phonon dispersion calculations. Films in the 1T phase reveal different CDW patterns in the first layer compared to the second. Interestingly, we find the second layer of the 1T film shows a CDW pattern with 4a × 4a periodicity which is the 2D version of the bulk CDW observed in this compound. Our phonon dispersion calculations confirm the presence of a soft phonon at the correct wave vector that leads to this CDW. In contrast, the first layer of distorted 1T phase films shows a strong stripe feature with varying periodicities, while the second layer displays no observable CDW pattern. Finally, we find that the monolayer 1T VSe2 film is weakly ferromagnetic, with ∼3.5 μB per unit similar to previous reports.

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I. INTRODUCTION

Two-dimensional (2D) materials such as graphene have attracted much recent attention due to the novel electronic and physical properties that accompany reduced dimensionality. While graphene has a large range of potential applications, the lack of an electronic band gap limits its use in optical and semiconducting devices [1]. Another 2D material system of interest is transition metal dichalcogenides (TMDs). TMDs are layered materials containing two chalcogen atoms per transition metal atom, displaying strong intralayer bonding and weak van der Waals interlayer bonding. The weak interlayer bonding of TMDs facilitates control of film thickness via growth or exfoliation down to submonolayer. As TMDs are reduced to 2D, novel physics often emerges such as itinerant magnetism [2], an indirect to direct band-gap transition [3,4], quantum spin Hall effect [5], and strongly enhanced charge density wave (CDW) order [6]. This breadth of phenomena makes 2D TMDs a promising platform both for the development of next generation devices and important fundamental studies.

VSe2 has recently attracted much interest due to reports of emergent room temperature ferromagnetism in the 2D limit. This finding, however, remains controversial as several theoretical [7–10] and experimental [11–13] studies both confirm and deny the possibility of a ferromagnetic phase in this compound. The films are also interesting due to the variety of CDW patterns observed which are distinct from the bulk sample [14,15], raising questions about the role of Fermi surface nesting and phonons in CDW formation. Bulk VSe2 is paramagnetic [16–18] and noteworthy for being one of the few materials exhibiting a three-dimensional CDW (4a × 4a × 3.1c) [19]. The bulk material has been shown to be stable in 1T octahedral structure [Figs. 1(a) and 1(b)]. In general, however, TMDs can also be found in 2H trigonal prismatic structure and distorted 1T structure [Figs. 1(c) and 1(d)], including 1T' orthorhombic and 17' monoclinic, which occurs when the chalcogen atoms in the 1T phase dimerize [1,20]. Most reports of 2D VSe2 films have been carried out on the 1T phase, leaving the synthesis and electronic properties of other polymorphs largely unexplored.
which is a precursor to the distorted 1\textsuperscript{st} striped discommensurate CDW in the monolayer structure. For the higher growth temperature of 450 °C, a two-dimensional projection of the commensurate bulk CDW patterns show that the monolayer VSe\textsubscript{2} samples grown at low temperature are weakly ferromagnetic with Curie temperature less than 1 \textdegree C. Intriguingly, the 1.5-layer VSe\textsubscript{2} samples grown at higher temperature also exhibit ferromagnetic behavior at room temperature or below, but with a lower magnetic moment per V atom.

In this paper we report the molecular beam epitaxy (MBE) growth of VSe\textsubscript{2} films on bilayer graphene (BLG)/6H-SiC (0001) substrates at two different growth temperatures, resulting in two distinct polymorphs. The synthesis procedures were characterized with reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) to discern structural and electronic properties compared to bulk VSe\textsubscript{2} crystals. At lower growth temperatures of 200 °C, the monolayer film displays the 1\textsuperscript{st} phase, which exhibits unique incommensurate CDW patterns in contrast to previous reports. Interestingly, the CDW in the bilayer is a two-dimensional projection of the commensurate bulk CDW structure. For the higher growth temperature of 450 °C, a striped discommensurate CDW in the monolayer is revealed which is a precursor to the distorted 1\textsuperscript{st} phase [Figs. 1(c) and 1(d)] observed in the bilayer. Our magnetization measurements show that the monolayer VSe\textsubscript{2} samples grown at low temperature are weakly ferromagnetic with Curie temperature higher than 300 K. Intriguingly, the 1.5-layer VSe\textsubscript{2} samples grown at higher temperature also exhibit ferromagnetic behavior at room temperature or below, but with a lower magnetic moment per V atom.

II. METHODS

VSe\textsubscript{2} thin films were grown on bilayer graphene (BLG) on SiC using a home-built MBE system with a base pressure <1 × 10\textsuperscript{−9} Torr. For BLG growth, 6H-SiC (0001) substrates were washed in acetone and isopropanol and then loaded into the MBE chamber. The substrates were degassed at 650 °C for 2–3 h, then flash annealed 45 times between 650 °C and 1300 °C. High-purity V (99.8%) and Se (99.999%) were evaporated from an e-beam evaporator and a dual-filament low-temperature Knudsen cell, respectively. The fluxes of V and Se were measured by a quartz crystal monitor, with the flux ratio kept between 1:20 and 1:30. The growth processes were monitored by in situ RHEED. The thin films grown at 200 °C and 450 °C are labeled low growth temperature (LGT) samples and high growth temperature (HGT) samples, respectively.

After growth, the samples were transferred to a low-temperature scanning tunneling microscope (STM) using a home-built “vacuum suitcase” to prevent the degradation of the sample quality. The vacuum during the transfer was less than 1 × 10\textsuperscript{−9} Torr. STM and scanning tunneling spectroscopy (STS) measurements were performed at 4 K. In the STM measurements, electrochemically etched and vacuum annealed tungsten tips were used. For comparison, bulk VSe\textsubscript{2} single crystals were cleaved in situ at a base pressure <2 × 10\textsuperscript{−9} Torr and transferred into the same low-temperature STM.

To carry out measurements of the films’ magnetic properties, they were capped with 10 nm of amorphous Se immediately after growth. The samples were then taken out of the MBE chamber and mounted into the Quantum Design Magnetic Properties Measurement System (MPMS). The magnetization M-H curves were measured in superconducting quantum interference device (SQUID) vibrating sample magnetometer (VSM) mode with an in-plane magnetic field. The magnetic moment per formula unit is roughly estimated by dividing the saturation magnetization, converted to Bohr magnetons, by the number of formula units which is obtained from the surface area, thickness, and volume of the VSe\textsubscript{2} unit cell.

The first-principles calculations were carried out using the Vienna ab initio simulation package (VASP) [23,24] with the projected augmented wave (PAW) [25] potentials. The exchange-correlation functional was treated within the generalized gradient approximations (GGA) [26–30]. The cutoff energy used throughout the calculations was set to 400 eV. Atomic positions were optimized for each lattice constant value considered until the criteria for energy convergence for self-consistency was set at 10\textsuperscript{−6} eV/Å. The vacuum region along the z direction was set to approximately 15 Å to prevent interactions between the repeated monolayer/bilayer slabs under the periodic boundary condition. A Γ-centered Monkhorst-Pack [31] grid of 12 × 12 × 1 in the first Brillouin zone was used for calculating atomic structures and lattice relaxations. However, a denser grid of 36 × 36 × 1 was used for density of states calculations.

To investigate lattice dynamics, phonon dispersion is calculated using the supercell method as implemented in the PHONOPY code [32]. We consider 4 × 4 supercells and 1 × 1 cells for phonon calculations of 1\textsuperscript{st} and 4 × 4 CDW structures, respectively. Crystal structure of 4 × 4 CDW is determined by displaying atoms of a 4 × 4 perfect 1\textsuperscript{st} supercell along the eigenvector of a soft mode at a commensurate q point followed by atomic relaxation in the fixed supercell.

III. RESULTS AND DISCUSSION

Previous works on VSe\textsubscript{2} thin films report several distinct CDW patterns, as well as the existence and absence of ferromagnetism, which highlight the sensitivity of resultant...
film properties to growth parameters and substrate choices [11,13–15]. The exploration of the substrate and synthesis parameter space is therefore important in fine-tuning film properties. BLG was chosen as a substrate in hopes of approximating a free-standing film for two reasons. First, as graphene does not have a Fermi surface near the \( \Gamma \) point where VSe\(_2\) has a holelike band, substrate-film interaction could be minimized. Second, a large lattice mismatch between graphene and Se lattice encourages weak van der Waals bonding between BLG and the film. However, a previous study on VSe\(_2\) thin films [14] reported a dependence of the CDW structure on the relative angle between the substrate and film. Therefore, heterostructure effects cannot be completely neglected.

Two different synthesis conditions were used in our experiments; LGT, where the substrate was held at 200 °C, and HGT, where the substrate was held at 450 °C. The BLG grown on SiC is atomically flat, observed by RHEED, whose pattern is shown in Fig. 2(a). High-quality 2D growth is confirmed with sharp streaks in RHEED images [Fig. 2(b)], which are seen for the 0.5 layer at both growth temperatures. A growth rate of 0.06 layer/min allowed for control of film thickness. Since our studies focused on the first and second layers, we aimed for 1.5-layer film growth in both conditions which allows us to see both the first and the second layers. Both growth procedures produced large terraces of VSe\(_2\) on BLG [Figs. 2(e) and 2(g)].

The 1.5-layer LGT film, as shown in Fig. 2(c), displays the same RHEED pattern as the 0.5-layer film. The absence of a graphene RHEED pattern indicates an almost complete coverage of the substrate by the film. STM images of the 1.5-layer LGT film show a triangular Se lattice with lattice constant \( a = 0.34 \) nm [Figs. 3(a) and 3(d)], which is consistent with the bulk lattice constant as well as with other reports of VSe\(_2\) films [19,33]. In the region where multiple layers (including a small exposed BLG area) are visible, a line-cut profile across the edges is shown in Fig. 2(f) [the orange line in Fig. 2(e)]. A step height of 0.6 nm is seen between the first and second layer of VSe\(_2\), consistent with the \( c \)-axis lattice constant in the bulk of 0.61 nm [33]. On the other hand, the height difference between BLG and the first layer is 0.8 nm, which is slightly larger than the lattice constant \( c \) in the bulk VSe\(_2\). This is consistent with previous experimental reports [34,35] and can be identified as a monolayer since 0.8 nm is significantly closer to monolayer (0.61 nm) thickness than the two-layer thickness (1.22 nm). This difference in heights is likely due to interfacial effects.

STM images on the monolayer reveal several 2D CDW patterns in different areas (Supplemental Fig. 1 in the Supplemental Material [36]). The most frequently observed CDW is shown in Fig. 3(a) with CDW vectors of \( q_1 = 4.2a \) by \( q_2 = 4.6a \), approximately. This 2D CDW order forms an oblique lattice with an angle of approximately \( 114^\circ \) and displays minor variations in the angle and magnitude in different areas on the sample. The 2D CDW is concomitant with a strong incommensurate 1D stripe order of periodicity \( d = 0.79 \) nm equivalent to \( 2.33a \). The 1D order occurs at an angle that is approximately \( 30^\circ \) deviated from one of the Se lattice directions and is observed in all monolayer scans with the same angle and periodicity. The 1D feature may perhaps be attributed to a mixture of \( \sqrt{3}a \times \sqrt{7}a \) and \( \sqrt{3}a \times 2a \) CDW patterns. Previous reports of coexisting \( \sqrt{3}a \times \sqrt{7}a \) and \( \sqrt{3}a \times 2a \) CDW orders in VSe\(_2\) thin films [14] show peaks in the Fourier transform at a period of 2.28\( a \) which is close to the 2.33\( a \) periodicity observed by us in this region. The observation of coexisting CDWs is also consistent with first-principles phonon calculations for the 1T monolayer which show multiple potential CDW instabilities corresponding to commensurate and incommensurate \( 4a \times 4a \) (\( q_1 \) and \( q_2 \)), \( \sqrt{3}a \times \sqrt{7}a \) \((q_1)\), and \( \sqrt{7}a \times \sqrt{7}a \) \((q_3)\) structures [Fig. 3(b)]. We note that consistent with previous studies on VSe\(_2\) films, the monolayer does not show a moiré pattern which based on the lattice mismatch would be expected to have a \( 3a \times 3a \) periodicity. Finally, as shown in Fig. 3(c), a measurement of the density of states of the LGT monolayer by STM spectroscopy shows a gap of 52 ± 2 meV centered at the Fermi energy (also see Supplemental Fig. 2 [36]). Using a Bardeen–Cooper–Schrieffer

![Image](https://via.placeholder.com/150)

**FIG. 2.** Characterization of epitaxially grown VSe\(_2\) films by RHEED and STM. (a)–(d) RHEED pattern of BLG grown on 6H-SiC (0001) substrate, LGT and HGT films after 0.5-layer growth, LGT film after 1.5-layer deposition, and HGT film after 1.5-layer deposition. In (d) the extra streaks are marked by the orange arrows, which indicate the formation of the distorted 1T phase. (e), (g) Large STM topographies of 1.5-layer LGT and 1.5-layer HGT samples (150 nm \( \times \) 150 nm). (f), (h) Height profiles of the orange lines in (e), (g), respectively.
Surprisingly, the bilayer LGT sample hosts a CDW which resembles the bulk (Supplemental Fig. 4(a) [36]) displaying a commensurate 2D CDW pattern with $4a \times 4a$ periodicity [Fig. 3(d)]. Our phonon dispersion calculations [Fig. 3(e)] display three noticeable imaginary modes at $q_1$, $q_2$, and $q_3$. The mode at $q_1 \sim -1/2 \Gamma M$ has the largest negative frequency, and the displacing atom along the eigenvector of this mode results in a $4a \times 4a$ commensurate CDW structure. According to our calculation, the energy of this CDW state is $11 \text{ meV/atom}$ lower than that of the normal state. Thus, the $4a \times 4a$ CDW is indeed preferred in this system and the electron-phonon interaction plays an important role in its formation. Moving on to density of states measurements as shown by the blue curve in Fig. 3(f), we observe a large peak around $-22 \text{ meV}$ which is absent in the monolayer (Supplemental Fig. 5 [36]). To understand these data, we performed the first-principles calculations for the bilayer which is shown as the red curve in Fig. 3(f). The calculation fits reasonably well with the experimental data in terms of the energy scales of some of the important features. The peaks around $-25$ and $+62 \text{ meV}$ in the calculated density of states match the experimental peaks at $-22$ and $+60 \text{ meV}$. These arise from the $3d$ bands of V which are split due to the bilayer coupling and this assignment of the peak to V $d$ bands is confirmed by a comparison of the second-layer spectrum and the STM measured density of states (DOS) of the bulk sample (Supplemental Fig. 4(b) [36]).

A similar peak feature appears in the bulk but is sharper in the bilayer. A comparison of the bilayer to the monolayer in the LGT films thus demonstrates the significant impact of just one additional layer of growth on phonons as well as the band structure.

The HGT films obtained by changing the substrate growth temperature by a few hundred degrees exhibit drastically different properties. Before proceeding we note that even though the growth temperature is higher, by keeping the Se to V flux ratio very high, between 20 and 30, we avoid Se loss in the films. Correspondingly our topographies of all HGT films show the expected hexagonal Se lattice with no missing Se atoms. We start by studying the HGT monolayer. While RHEED images of the monolayer look identical to the LGT [Fig. 2(b)], STM images show a strong 1D stripe feature with varying periodicity. As seen in Fig. 4(a), the stripes occur along a lattice direction with periodicities of either 4, 5, or 6 times the lattice. Along the direction of stripes, the lattice constant, 0.34 nm, is the same as the one in LGT samples. Taking a line cut along the stripe direction [Fig. 4(e)], it is clear that the distances between two adjacent atoms are uniform. However, along the other two lattice directions [the height profile shown in Fig. 4(f)], it appears that the atoms are not evenly spaced and the average atomic separation, 0.31 nm, is almost 10% smaller than the one along the stripes in LGT samples. To confirm the universality of this observation, we obtained topographies in different areas with stripes along various directions. We find that the difference between lattice constants along and across the stripe direction is consistent. Interestingly, the spectra on bright and dark stripes are different (Supplemental Fig. 6 [36]) which suggests an electronic origin (such as a CDW) for the stripes. One-dimensional CDWs with varying periodicities have been explained using the theory of discommensurations, where
slightly incommensurate CDWs become commensurate over a region and undergo a phase slip between regions to lower their energy [37]. Discommensurate CDWs have been previously observed in bulk NbSe$_2$, caused by local strain [38]. In our HGT VSe$_2$ samples, we speculate that strain induced by synthesis conditions or growth specific heterostructure interactions may cause dimerization and discommensurate CDW in the monolayer. We note that a discommensurate 1D CDW has not been observed in previous VSe$_2$ monolayer studies.

As the growth progresses from monolayer to bilayer, accompanying the HGT bilayer growth are additional streaks in the RHEED image, as shown in Fig. 2(d). These streaks occur halfway between the center spot and the most prominent RHEED streaks, implying the onset of a $2a$ structural periodicity. Correspondingly, STM images of the HGT bilayer show a one-dimensional pattern along a lattice direction [Fig. 4(c)]. The RHEED pattern, STM images, and previous reports on 1T TMDs [5,39] lead us to conclude that the bilayer HGT film grows in the distorted 1T phase. As illustrated in Figs. 1(e) and 1(d), the V atoms in the distorted 1T phase dimerize, causing the bond lengths of neighboring Se atoms to change. Se atoms in the center of a V dimer are slightly elevated in the interlayer direction and Se atoms in between dimers are slightly depressed. This elevation and depression are responsible for the contrast seen in the STM image and are obviously exhibited in a line-cut profile Fig. 4(g). As shown in Supplemental Fig. 7 [36], the spectra are almost identical across the stripes, consistent with our RHEED analysis that the stripes result from lattice distortion.

Though the structures of monolayer and bilayer are remarkably different, their spectra are qualitatively similar [Figs. 4(b) and 4(d)]. There are three peaks above the Fermi energy at approximately the same positions in the two layers, although their relative intensities are different. Below the Fermi energy, however, the density of states curve in the second layer is slightly different from the monolayer. We also carried out first-principles calculation for 1T and 1T$_d$ phase bilayer VSe$_2$. The comparison between experiment and calculation is shown in Supplemental Fig. 8 [36]. We find that unlike the calculations for the 1T films, the agreement between theory and experiment is not very good. One possible explanation is that the distorted 1T samples grow on a layer of strained 1T VSe$_2$, which the calculation does not capture.

Besides the electronic and structural properties of VSe$_2$ films in the atomic limit, the magnetic properties are also of significant interest. According to the $M$-$H$ curves from MPMS measurements of our samples at different temperatures, the monolayer LGT VSe$_2$ sample is ferromagnetic, with $\sim$3.5 $\mu_B$ per formula unit similar to previous reports [14] and the Curie temperature is higher than 300 K. Intriguingly, the 1.5-layer HGT VSe$_2$ samples also exhibit a ferromagnetic behavior at room temperature or below, but with a weaker magnetic moment, $\sim$1.3 $\mu_B$ per formula unit. More details are displayed in Supplemental Fig. 9 [36].

IV. CONCLUSION

In this paper we report the growth of VSe$_2$ films on BLG/SiC at 200 °C and 450 °C, labeled LGT and HGT, respectively. The LGT films show 2D incommensurate CDW patterns in the monolayer, with a periodicity that is different from those of previous reports. This evolves into a commensurate $4a \times 4a$ CDW in the bilayer that is similar to the bulk. The HGT films show unique phenomenology when compared to the LGT films and previous reports. The HGT monolayer displays a 1D discommensurate CDW, indicative of strain. The HGT bilayer grows in the distorted 1T phase, which has, so far, rarely been reported in VSe$_2$ and is likely stabilized by interactions with the monolayer. Our results on the HGT films allow for the study of two interesting phenomena in VSe$_2$ films: a discommensurate 1D CDW and the distorted 1T phase. Specifically, the distorted 1T phase provides more possibilities for synthesizing different phases of TMDC thin films and realizing alternative heterostructures with potentially exotic properties.

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[1] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, Nat. Rev. Mater. 2, 17033 (2017).
[2] T. Danz, Q. Liu, X. D. Zhu, L. H. Wang, S. W. Cheong, I. Radu, C. Ropers, and R. I. Tobey, J. Phys. Condens. Matter 28, 356002 (2016).
[3] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).
[4] Y. Zhang, T.-R. Chang, B. Zhou, Y.-T. Cui, H. Yan, Z. Liu, F. Schmitt, J. Lee, R. Moore, Y. Chen et al., Nat. Nanotechnol. 9, 111 (2014).
[5] S. Tang, C. Zhang, D. Wong, Z. Pedramrazi, H.-Z. Tsai, C. Jia, B. Moritz, M. Claassen, H. Ryu, S. Kahn et al., Nat. Phys. 13, 683 (2017).
[6] X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, and K. F. Mak, Nat. Nanotechnol. 10, 765 (2015).
[7] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, and B. Huang, ACS Nano 6, 1695 (2012).
[8] S. Lebègue, T. Björkman, M. Klintenberg, R. M. Nieminen, and O. Eriksson, Phys. Rev. X 3, 031002 (2013).
[9] A. O. Fumega, M. Gobbi, P. Dreher, W. Wan, C. Gonzalez-Orellana, M. Peña-Díaz, C. Rogero, J. Herrero-Martin, P. Gargiani, M. Ily et al., J. Phys. Chem. C 123, 27802 (2019).
[10] P. Coelho, K. Nguyen-Cong, M. Bonilla, S. K. Kolekar, M.-H. Phan, J. Avila, M. C. Asensio, I. I. Oleynik, and M. Batzill, J. Phys. Chem. C 123, 14089 (2019).
[11] M. Bonilla, S. Kolekar, Y. Ma, H. C. Diaz, V. Kalappattil, R. Das, T. Eggers, H. R. Guterrez, M.-H. Phan, and M. Batzill, Nat. Nanotechnol. 13, 289 (2018).
[12] K. Xu, P. Chen, X. Li, C. Wu, Y. Guo, J. Zhao, X. Wu, and Y. Xie, Angew. Chem., Int. Ed. 52, 10477 (2013).
[13] J. Feng, D. Biswas, A. Rajan, M. D. Watson, F. Mazzola, O. J. Clark, K. Underwood, I. Markovic, M. McLaren, A. Hunter et al., Nano Lett. 18, 4493 (2018).
[14] G. Duvjur, B. K. Choi, I. Jang, S. Ulstrup, S. Kang, T. Thi Ly, S. Kim, Y. H. Choi, C. Jozwiak, A. Bostwick et al., Nano Lett. 18, 5432 (2018).
[15] D. Zhang, J. Ha, H. Baek, Y.-H. Chan, F. D. Natterer, A. F. Myers, J. D. Schumacher, W. G. Cullen, A. V. Davydov, Y. Kuk et al., Phys. Rev. Mater. 1, 024005 (2017).
[16] C. Van Bruggen and C. Haas, Solid State Commun. 20, 251 (1976).
[17] M. Bayard and M. Sienko, J. Solid State Chem. 19, 325 (1976).
[18] S. Barua, M. C. Hatean, M. Lees, and G. Balakrishnan, Sci. Rep. 7, 10964 (2017).
[19] A. Pasztor, A. Scarfato, C. Barreteau, E. Giannini, and C. Renner, 2D Mater. 4, 041005 (2017).
[20] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nat. Nanotechnol. 7, 699 (2012).
[21] P. Chen, W. W. Pai, Y.-H. Chan, V. Madhavan, M.-Y. Chou, S.-K. Mo, A.-V. Fedorov, and T.-C. Chiang, Phys. Rev. Lett. 121, 196402 (2018).
[22] Y. Umemoto, K. Sugawara, Y. Nakata, T. Takahashi, and T. Sato, Nano Res. 12, 165 (2019).
[23] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[24] G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
[25] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[26] A. Rajagopal and J. Callaway, Phys. Rev. B 7, 1912 (1973).
[27] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[28] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
[29] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[30] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[31] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[32] A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).
[33] J. A. Wilson and A. Yoffe, Adv. Phys. 18, 193 (1969).
[34] Y. Zhao, J. Qiao, P. Yu, Z. Hu, Z. Lin, S. P. Lau, Z. Liu, W. Ji, and Y. Chai, Adv. Mater. 28, 2399 (2016).
[35] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, Adv. Funct. Mater. 22, 1385 (2012).
[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.102.115149 for more details about experimental data and calculations.
[37] W. McMillan, Phys. Rev. B 14, 1496 (1976).
[38] A. Soumyanarayanan, M. M. Yee, Y. He, J. Van Wezel, D. J. Rahn, K. Rossnagel, E. W. Hudson, M. R. Norman, and J. E. Hoffman, Proc. Natl. Acad. Sci. USA 110, 1623 (2013).
[39] S. Tang, C. Zhang, C. Jia, H. Ryu, C. Hwang, M. Hashimoto, D. Lu, Z. Liu, T. P. Devereaux, Z. X. Shen et al., APL Mater. 6, 026601 (2018).