Spin polarization driven by a charge-density wave in monolayer 1T-TaS₂

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Using first-principles calculations, we investigate the electronic and vibrational properties of monolayer *T*-phase TaS₂. We demonstrate that a charge-density wave is energetically favorable at low temperature, similar to bulk 1T-TaS₂. Electron-phonon coupling is found to be essential for the lattice reconstruction. The charge-density wave results in a strong localization of the electronic states near the Fermi level and consequently in spin polarization, transforming the material into a magnetic semiconductor with enhanced electronic correlations. The combination of inherent spin polarization with a semiconducting nature distinguishes the monolayer fundamentally from the bulk compound as well as from other two-dimensional transition metal dichalcogenides. Monolayer *T*-phase TaS₂ therefore has the potential to enable two-dimensional spintronics.

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Two-dimensional materials often show exotic physical properties, which are distinctly different from those of their bulk counterparts. Not surprisingly, many possible applications for this class of materials therefore have been put forward, in particular, in nanoelectronics, sensing, and photonics. Monolayers of transition metal dichalcogenides, such as MoS₂ and WSe₂, nowadays are receiving immense interest [1–4]. Various bulk transition metal dichalcogenides, such as 1T-TaS₂, 2H-TaSe₂, and 1T-TiSe₂, are known to be subject to instabilities against charge-density waves (CDWs), i.e., periodic modulations of the electronic charge density accompanied by periodic distortions of the crystal lattice [5–27].

Among these compounds, 1T-TaS₂ was studied extensively in the last four decades due to its rich phase diagram. Different phase transitions occur as a function of the temperature: [5,9,16] An incommensurate CDW develops below 550 K, which, upon further cooling, becomes almost commensurate around 350 K. Finally, a commensurate CDW is formed below 180 K with a $\sqrt{13} \times \sqrt{13}$ periodic lattice distortion, the so-called “Star-of-David” cluster. Superconductivity appears under pressure [16]. The origin of the CDW, the pseudogapped Fermi surface, and the coexistence of CDW and superconducting phases have motivated many studies, both experimental and theoretical. In contrast to these efforts on bulk 1T-TaS₂, the monolayer *T* phase of TaS₂ has received little attention, probably because it could not be fabricated until very recently [28]. We investigate in the following the electronic and vibrational properties of this phase by first-principles calculations. We will demonstrate that, also in the monolayer material, a CDW is realized at low temperature. Importantly, the electronic states near the Fermi level strongly localize by the specific lattice reconstruction, which results in spin polarization and transforms the system from a metal into a magnetic semiconductor. This combination of material properties gives rise to an exciting alternative to the existing two-dimensional transition metal dichalcogenides, in particular, in spintronics.

All structure relaxations and band structure calculations are performed using the Vienna *ab initio* simulation package [29] and the generalized gradient approximation. The kinetic energy cutoff is set to 400 eV. For the bulk compound $12 \times 12 \times 8$ and $4 \times 4 \times 8$ *k* meshes, respectively, are employed for the unit cell and $\sqrt{13} \times \sqrt{13} \times 1$ supercell. On the other hand, $16 \times 16 \times 1$ and $8 \times 8 \times 1$ *k* meshes are used for the monolayer in these two cases. Heavy Ta requires the inclusion of spin-orbit coupling in the band structure calculations. The ionic relaxation is stopped when the forces on all atoms have declined to less than 0.01 eV/Å. For the layered structure of bulk 1T-TaS₂ a damped van der Waals correction [30] is adopted to reproduce the experimental lattice constants. Moreover, phonon spectra are calculated within linear response theory [31], using $10 \times 10 \times 1$ *q* meshes for the dynamical matrices. The force constants are obtained by Fourier transformation and interpolation to arbitrary points in the Brillouin zone. Bulk 1T-TaS₂ with space group $P\bar{3}m1$ has experimental lattice parameters of $a = 3.36$ Å and $c/a = 1.74$. The unit cell contains three atoms, with Ta at (0,0,0) and the two S atoms at $\pm(1/3, 2/3, z)$, where $z = 0.242$. For the monolayer system our structure relaxation results in a lattice constant of $a = 3.37$ Å (where a 17 Å thick vacuum layer is adopted along the *c* axis). This corresponds to a distance between the two S layers of 3.06 Å.

Turning to the electronic structure, we first compare the band structures and densities of states of bulk 1T-TaS₂ and monolayer *T*-phase TaS₂ [see Figs. 1(a) and 1(b)]. The band structures near the Fermi level are similar and both reflect metallicity. Due to the presence of inversion symmetry, there is no band splitting throughout the Brillouin zone, in contrast to monolayer MoS₂, for example. The total and partial densities of states in Figs. 1(c) and 1(d) demonstrate that for both systems the states near the Fermi level are mostly due to the Ta *d* orbitals with some smaller S *p* contributions. The strong similarities between the electronic structures obtained for the bulk and monolayer cases can be explained by the quasi-two-dimensional nature already present in bulk 1T-TaS₂. The S-Ta-S slabs are bonded by van der Waals forces, which are much weaker than the intraslab chemical interactions.

Since bulk 1T-TaS₂ develops, at low temperature, a CDW accompanied by periodic lattice distortions, it is a natural

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FIG. 1. (Color online) Band structures and densities of states (per formula unit) of (a), (c) bulk 1T-TaS₂ and (b), (d) monolayer *T*-phase TaS₂.

question whether a similar transition will occur in monolayer *T*-phase TaS₂. To investigate the stability of the monolayer, we study the phonon spectrum. A series of calculations has been carried out at $Q_{\text{CDW}} = (0.277, 0.160, 0)$ with different k meshes and Gaussian smearings. The latter parameter characterizes the electronic temperature of the system and therefore determines the electron-phonon coupling. According to Fig. 2(a), the phonon frequencies are converged for a $20 \times 20 \times 1$ k mesh combined with a Gaussian smearing of 0.01 Ry, for which we calculate the phonon spectra along high symmetry lines [see Fig. 2(b)]. Two of the three acoustic branches correspond to vibrations within the plane of the two-dimensional structure, i.e., the longitudinal acoustic (LA) and transverse acoustic (TA) modes, and the other to out-of-plane vibrations (ZA). Phonon anomalies are found in one of the acoustic branches, the most pronounced being located at $(0.287, 0.166, 0) \approx Q_{\text{CDW}}$. This indicates that the ideal structure of monolayer *T*-phase TaS₂ is unstable at low temperature.

Commonly the Peierls picture is adopted to explain the CDW phase of bulk 1T-TaS₂. In a perfectly one-dimensional system a CDW lowers the energy of the electrons near the Fermi level when a lattice vector connects the two points of the Fermi surface. In order to identify the origin of the CDW

phase in monolayer *T*-phase TaS₂, we calculate the real and imaginary parts of the noninteracting electronic susceptibility using the constant matrix element approximation [32]. The imaginary part (nesting function) is shown in Fig. 3(a). Besides the divergence at the Γ point, no pronounced peaks appear throughout the Brillouin zone, only weak peaks near Q_{CDW} and the Γ and K points. This implies that Fermi surface nesting is not relevant to the CDW instability. On the other hand, the real part in Fig. 3(b) shows sharp peaks near Q_{CDW} , matching exactly the wave vector of the most pronounced anomaly in Fig. 2(b). Therefore, the CDW instability is due to the electron-phonon coupling [32].

The $\sqrt{13} \times \sqrt{13}$ lattice reconstruction in the CDW phase of bulk 1T-TaS₂ results in metal clusters with one Ta atom in the center of two rings of six Ta atoms each, with a substantial charge transfer from the outer ring towards the center. It is reasonable to check whether monolayer *T*-phase TaS₂ is subject to a reconstruction with the same periodicity. Relaxation of the atomic positions shows that the total energy can, in fact, be lowered by 0.030 eV per formula unit, which is slightly more than in the case of the bulk compound (0.027 eV per formula unit). After optimization, the structure reveals substantial displacements of the Ta atoms of up to 0.26 Å.

FIG. 2. (Color online) (a) Phonon frequency at Q_{CDW} as a function of the Gaussian smearing for different k meshes. (b) Phonon spectra of monolayer T -phase TaS_2 for a $20 \times 20 \times 1k$ mesh and a Gaussian smearing of 0.01 Ry.

For the CDW phase, the band structure of bulk $1T$ - TaS_2 is shown in Fig. 4(a) and that of the monolayer in Fig. 4(b). In contrast to the ideal system, a finite magnetic moment emerges (also if the spin-orbit coupling is turned off) as a result of the periodic lattice distortion. This spin polarization is reflected in the band structure by two flat bands of opposite spin above and below the Fermi level. A similar feature does not appear in bulk $1T$ - TaS_2 , which is diamagnetic according to Ref. [5], demonstrating that the spin polarization is a consequence of the two-dimensional geometry. In the bulk system the layer-layer interaction delocalizes the in-plane states, which suppresses spin polarization. The energy gap between the two flat bands in Fig. 4(b) amounts to 0.12 eV and the absolute value of the z component of the spin is the same, as indicated by the size of the circles. Orbital projections of the density of states for both the bulk and monolayer systems in Figs. 4(c) and 4(d) show that the states around the Fermi level are largely due to the Ta $d_{3z^2-r^2}$ orbitals, with only weak hybridization with the S p orbitals. Due to the spin polarization and the induced band splitting, monolayer T -phase TaS_2 becomes

a magnetic semiconductor. The spontaneous magnetization, which is not present in other two-dimensional transition metal dichalcogenides, is highly promising because of a large variety of applications in spintronics.

To illustrate the reconstruction pattern, we plot in Fig. 5(a) the charge-density difference between the ideal and CDW phases. We observe charge accumulation within the Ta cluster and shifts of the outer Ta atoms towards the center. Figure 5(b) shows the magnetization density (z component of the spin) in real space and demonstrates strong localization in the center of the cluster. We note that the band splitting in the vicinity of the Fermi level is caused solely by the spin polarization and not by a strong on-site electron-electron interaction (which is not taken into account in the generalized gradient approximation). Previous results on bulk $1T$ - TaS_2 have been interpreted in the sense that both lattice distortion and electron correlations are essential for the opening of a band gap and therefore for the semiconducting nature of the CDW phase [16]. For the monolayer system we find that the gap opening and electron localization are consequences of the lattice distortion only. The

FIG. 3. (a) Imaginary and (b) real part of the electronic susceptibility of ideal monolayer T -phase TaS_2 . White and black represent large and small values, respectively. The Brillouin zone boundaries are highlighted and arrows indicate Q_{CDW} .

FIG. 4. (Color online) Band structures and densities of states (per formula unit) of (a), (c) bulk 1T-TaS₂ and (b), (d) monolayer *T*-phase TaS₂ in the CDW phase. The size of the circles in (b) is proportional to the z component of the spin and the red (blue) color represents positive (negative) values.

FIG. 5. (Color online) (a) Charge-density difference between the ideal and CDW phases of monolayer *T*-phase TaS₂. The isosurface value is 0.02 electrons/Å³. (b) Magnetization density (z component of the spin) in the CDW phase. The isosurface value is 0.001 electrons/Å³. Ta and S atoms are shown in blue and yellow colors, respectively.

fact that the gap opening results indirectly from the induced spin polarization is different from the conventional Peierls picture. Of course, since the states around the Fermi level turn out to be strongly localized, electron correlations will be enhanced and the experimental band gap can be expected to be larger than predicted by our calculations. However, the origin of the metal to magnetic semiconductor phase transition in monolayer *T*-phase TaS₂ is the electron-phonon coupling.

In conclusion, we have investigated the electronic and vibrational properties of monolayer *T*-phase TaS₂ by first-principles calculations. Our results demonstrate that the formation of a CDW is energetically favorable at low temperature. In the CDW phase the electronic states near the Fermi level are strongly localized, which explains the formation of significant magnetic moments. In Ref. [33] distorted monolayer *T*-phase

TaS₂ was found to be a Mott insulator. We obtain a similar electronic structure (except for the size of the energy gap) without including an on-site Coulomb interaction. Since the total energy difference between the ideal and distorted phases of monolayer *T*-phase TaS₂ is larger than in the case of the bulk compound, it can be expected that the transition temperature is higher than 180 K. The semiconducting nature combined with the spin polarization revealed by our calculations calls for urgent experimental characterization of monolayer *T*-phase TaS₂ as an exciting alternative to the existing two-dimensional transition metal dichalcogenides, in particular, in spintronics.

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