Absence of ferromagnetism in VSe$_2$ caused by its charge density wave phase

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In this study we present a detailed \textit{ab initio} analysis of the magnetic properties of VSe$_2$. \textit{Ab initio} calculations in the so-called 1T structure yield a ferromagnetic phase as most stable, with a magnetic moment of about 0.6 $\mu_B$/V. According to our calculations, and based on the Stoner criterion for itinerant ferromagnets, this ferromagnetic state is on the verge of instability. We have modeled \textit{ab initio} the charge density wave state reported in the literature. This introduces a periodic lattice distortion leading to a supercell with periodicity $4a \times 4a \times 3c$ ($4a \times 4a$ for the monolayer) in which we have relaxed the atomic positions. We demonstrate that this structural rearrangement causes a strong reduction in the density of states at the Fermi level and the ground state of the system becomes non-magnetic. Experimental evidences that report a magnetic signal need to be understood on the light of this finding.

Since the discovery of graphene\cite{1} there has been an enormous scientific effort in the search and characterization of purely two-dimensional (2D) materials that could show new physical properties and lead to potential new applications. In particular, the family of layered transition metal dichalcogenoides (TMDs) has been widely studied over the past years\cite{2–5}.

Very recently, ferromagnetism has been observed in a purely 2D material\cite{6}, and since then, the field of ferromagnetic 2D materials has gained momentum with the appearance of various families of layered, van der Waals bonded materials that remain ferromagnetic when exfoliated to the ultrathin limit\cite{7, 8}.

Vanadium diselenide (VSe$_2$) is a TMD that crystallizes naturally in a trigonal (T) phase. This consists of V atoms 6-fold coordinated by Se atoms forming layers in the (0001) direction (see Fig. 1). Van der Waals forces are responsible for the weak bonding between adjacent layers. As many other materials of that sort, VSe$_2$ is relatively easy to exfoliate\cite{9} or grow\cite{10} till the single and few-layer limit.

It has been reported that various TMDs show a charge density wave (CDW) phase at low temperatures\cite{11, 12}. In the case of VSe$_2$ this phase appears below 110 K\cite{13}. That critical temperature increases when going to the 2D scenario\cite{9} and also when pressure is applied\cite{14}. Signatures of the transition are seen in transport properties such as resistivity\cite{15} or thermopower\cite{16}. A symmetry breaking of the space group has been demonstrated to occur if a CDW transition exits\cite{17}. VSe$_2$ belongs to the P-3m1 space group in the normal state (NS), whereas a commensurate $4a \times 4a \times 3c$ supercell arises in the CDW state\cite{17, 18, 19} that occurs at low temperatures. This kind of periodic lattice distortion introduces extra reflections in the diffraction patterns\cite{20}. Strain engineering\cite{21} or atom intercalation\cite{22} can be used to change the modulation of the CDW supercell.

The T-phase of VSe$_2$, the one that we are going to study, presents a metallic behaviour in both the NS and the CDW state\cite{23} and also when going to the 2D limit\cite{9}. Experiments report a paramagnetic behaviour of bulk VSe$_2$\cite{15, 23, 24}. When going to the monolayer case ferromagnetism (FM) is claimed to arise\cite{10}. However, a huge discrepancy in the saturation magnetization is seen between a VSe$_2$ monolayer grown on top of MoS$_2$ ($\sim 15 \mu_B$ per V atom)\cite{10} and the exfoliated VSe$_2$ few-layer ($\sim 0.3 \times 10^{-3} \mu_B$ per V atom)\cite{9}. Previous density functional theory (DFT) calculations of bulk and monolayer VSe$_2$ show that a FM phase is the most stable one\cite{26, 27}, but with values of the magnetic moment in strong disagreement with those experimentally obtained. Previous DFT-based \textit{ab initio} calculations show that perturbations to the system, such as strain, are able to destroy magnetism\cite{27}.

In this work, we will try to understand the magnetic properties of VSe$_2$ from an \textit{ab initio} perspective. For that sake, we have performed \textit{ab initio} electronic

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{(Color online.) Representation of the 1T-structure as experimentally described for VSe$_2$. V atoms are in red and Se atoms in green. Observe the layered structure, layers bond weakly via van der Waals forces.}
\end{figure}
structure calculations based on DFT\cite{28,29} using an all-electron full potential code (wien2k\cite{30}) on VSe$_2$. The exchange-correlation term used was the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof\cite{31} scheme for structural optimizations and to compute all the energetics presented. These calculations were performed with a converged k-mesh and a value of $R_{mt}k_{max} = 7.0$. The $R_{mt}$ value used was 2.12 in a.u. for both V and Se. Structural data was taken from Ref.\cite{32}. Transport properties have been calculated using the BoltzTrap2 code\cite{33}. This solves Boltzmann transport equation from first-principles calculations within the constant scattering time approximation. A denser k-mesh was used for this task.

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\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{(Color online.) Top view of VSe$_2$ bulk structures. V atoms are represented as big red spheres and Se atoms are shown in green. a) NS structure. It can be reduced to a three-atom unit cell that belongs to the P-3m1 space group. DFT predicts a FM ground state for it. b) CDW structure. A modulated $4a \times 4a \times 3c$ supercell appears in the CDW state. FM is absent in this situation.}
\end{figure}

The NS bulk structure in the P-3m1 space group can be seen in Fig. 2a. The top view shows the hexagonal symmetry. The calculations yield a FM ground state with a total moment of 0.6 $\mu_B$ per V atom. The total energy as a function of the magnetization can be seen as the blue dashed line in Fig. 3 with a somewhat broad minimum around that value of the magnetization.

To understand the origin and characteristics of this ferromagnetic ground state, we can think of VSe$_2$ as an itinerant electron system. In that case, we can use the phenomenological Stoner theory and we can apply the Stoner criterion to determine if the structure is FM or not. This makes a comparison between the energy gained by the system via a spin splitting compared to the kinetic energy cost produced by displacing minority-spin electrons into a higher-energy majority-spin band. Only when the overall energy gets reduced an itinerant electron system like this can become spontaneously magnetic. This is usually formulated in the following way:

\begin{equation}
\text{Stoner criterion} \begin{cases} 
\text{FM, if } I \cdot DOS(E_F) > 1, \\
\text{Non-magnetic, otherwise.}
\end{cases}
\end{equation}

where $I$ is the exchange energy between the Bloch d-band electrons, the so called Stoner parameter. It can be obtained from the energy vs magnetization curve\cite{35} plot in Fig. 3. The density of states at the Fermi level ($DOS(E_F)$) can also be computed \textit{ab initio} for a non-magnetic solution.

In Fig. 4 we show how the Stoner criterion gets satisfied or not as a function of the number of electrons introduced per formula unit in the system by plotting the product of $1 \times DOS(E_F)$. The Fermi level corresponds to $n = 0$ in the plot and moving to the right or the left implies hole or electron doping, respectively. The carrier concentration was calculated using a rigid band approximation by integrating the total density of states of the non-magnetic calculation. Applying (1) we observe that the NS structure is inside the FM part of the phase diagram since the product of the number of electrons times

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{(Color online.) Energy as a function of the magnetization for the bulk structures. Computed points in black. The blue dashed line corresponds to the NS structure. It presents a minimum at around 0.6 $\mu_B$ per V atom. The red line corresponds to the CDW structure. It can be seen that the minimum-energy configuration is non-magnetic.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig4.png}
\caption{(Color online.) Top view of VSe$_2$ bulk structures. V atoms are represented as big red spheres and Se atoms are shown in green. a) NS structure. It can be reduced to a three-atom unit cell that belongs to the P-3m1 space group. DFT predicts a FM ground state for it. b) CDW structure. A modulated $4a \times 4a \times 3c$ supercell appears in the CDW state. FM is absent in this situation.}
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the density of states at the Fermi level is larger than 1, but not by much. Let us recall that such product is about 2.5-3 for Fe, Ni, Co, the simplest itinerant ferromagnets. Any perturbation to this system that could cause a small reduction in the DOS at the Fermi level would lead to a non-magnetic situation to become stable. For example, previous ab initio studies have shown that a reduction of the FM moment can be achieved using strain engineering in this system, so that relatively small values of strain could make ferromagnetism disappear in VSe$_2$.

**FIG. 4:** (Color online.) Stoner criterion for the NS structure as a function of the number of electrons introduced per formula unit. When $I \cdot \text{DOS} > 1$ the system is said to be FM. VSe$_2$ in the NS is FM but somewhat close to a non-magnetic state being stable.

As mentioned above, VSe$_2$ presents a CDW state at low temperatures. It is known that a CDW state leads to gap openings around the Fermi level for particular values of the lattice momentum. Thus, the introduction of a periodic lattice distortion of that sort could have an effect in the calculated DOS at the Fermi level and hence in the magnetic properties of this itinerant electron system. In order to take this into account in our calculations, we have computed a $4a \times 4a \times 3c$ supercell. The periodicity of the distortion was chosen from the experimental evidences that exist of the nature of the CDW in this system at low temperatures. For such an enlarged unit cell, we have optimized all the atomic positions obtaining the structure depicted in Fig. 2 panel b). One can see that the short-range hexagonal symmetry, in particular for the V sublattice, is lost, with the nearest neighbouring V-V distance becoming largely distorted. This optimized CDW structure is $28$ meV per formula unit more stable than the NS structure, a sizable value. Our result in the CDW structure is that the DOS at the Fermi level is vastly reduced compared to the NS structure. This can be seen in Fig. 5 in which the CDW DOS($E_F$) (red line) is presented, being almost half that of the NS (blue dashed) one. This reduction of the DOS causes the FM moment to be quenched. Figure 3 shows the plot of the total energy as a function of the magnetization for the CDW state (red line), where the minimum is at zero moment, as opposed to the non-vanishing magnetization that is the ground state for the NS structure.

**FIG. 5:** (Color online.) DOS around the Fermi level for the bulk structures. DOS of the CDW is shown in red, while the blue dashed represents the DOS of the NS. There is a clear reduction of the DOS when the CDW is present. This contraction leads to the FM phase being unstable in the CDW state.

In order to give further evidences that the relaxed structure we have obtained can model reasonably well the CDW state found experimentally with a periodic lattice distortion in the form of a $4a \times 4a \times 3c$ supercell, we have computed the thermopower of both the NS and the CDW structures and compared it to the experimental literature. Figure 6 shows the calculated thermopower as a function of temperature for the CDW (red line) and the NS structure (blue dashed line), and compared it with the experimental data from Ref. 16 (black points). Experimentally, a significant drop in the thermopower is observed at the transition from the CDW at low temperatures to the NS above $100$ K. Our results show that, at any temperature, the Seebeck coefficient is higher for the CDW structure than for the NS one. This can be explained considering that the CDW phase opens pseudogaps in the Fermi surface and hence thermopower increases when gaps are opened around the Fermi level. If a crossover from the CDW at low temperatures to the NS structure about $100$ K is to be expected, then we can see that our calculations help understand the behavior found in the thermopower reasonably well.

The CDW phase is present in VSe$_2$ down to the monolayer limit, in that case even with a higher critical temperature. This strongly suggests that the periodic lattice distortion associated to it needs to be considered when studying its magnetic properties. For that reason, we have carried out calculations for the mono-
FIG. 6: (Color online.) Thermopower as a function of temperature for bulk VSe$_2$. The black points show the experimental measurements from Ref. [16]. The red line shows the calculated thermopower for the 4$a \times 4$a $\times 3$c supercell. It fits the experimental data at low temperatures, when the CDW is present. The blue dashed line shows the calculated thermopower for the P-3m1 cell. It fits the experimental data at high temperatures, when the NS is present.

layer as well. We have performed a similar calculation comparing the total energy of a monolayer with all the V-V distances being equal to a fully relaxed 4$a \times 4$a supercell where the V-V nearest neighbor distances become uneven. The latter is the ground state and the tendency towards magnetism gets drastically reduced.

Figure 7a shows the DOS for the NS (blue dashed line) and for the CDW (red line) monolayer structures. As happened for the bulk structure, the DOS($E_F$) is reduced when the CDW is present. Figure 7b shows the energy vs magnetization curves for the monolayer structures. While FM is clearly present in the NS (blue dashed line), it tends to vanish for the CDW (red line). A very shallow minimum is obtained at 0.25 $\mu_B$ per V atom, in the limit of the predicting capability. This, together with the narrow peak of the DOS at the Fermi level (any perturbation such as doping would decrease it, favoring a reduction of FM) are evidences that also at the monolayer limit, the CDW-like distortion destroys the overall tendency for magnetism in this system. If a magnetic signal is obtained experimentally either in the bulk samples or in the single-layer limit, its origin cannot be intrinsic to VSe$_2$, according to our ab initio calculations.

A comparison between the NS structures of the bulk and the monolayer reveals that decreasing dimensionality increases the DOS at the Fermi level. As we have been discussing, this is in general a mechanism to enhance the chances for itinerant ferromagnetism to be stable when going to the monolayer limit in similar systems. However, for the case of VSe$_2$ this increase is not sufficient due to the detrimental effect caused by the CDW state at low temperatures.

In conclusion, we have shown that DFT calculations predict that the ground state of VSe$_2$ presents a commensurate lattice distortion with a 4$a \times 4$a $\times 3$c supercell. This structure is shown to be related with the CDW phase that has been experimentally detected at low temperatures. Our calculations for such a ground state show that ferromagnetism is absent due to the distortion. Such a structural change can also help understanding the change in thermopower observed experimentally at the transition. Also in the monolayer limit, a periodic lattice
distortion \((4a \times 4a)\) associated to the CDW state destroys the FM phase. Our calculations suggest that the origin of the magnetic signal obtained for \(\text{VSe}_2\) cannot be intrinsic to the material, either in the bulk or in the single-layer limit.

The results that we have shown for \(\text{VSe}_2\) could be extended to similar systems in which a CDW appears. They demonstrate the importance of considering the correct ground state structure when performing ab initio magnetic studies in this kind of compounds.

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