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Thickness-dependent magneto-optical effects in hole-doped GaS and GaSe multilayers: a first-principles study

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Keywords: magneto-optical Kerr effect, magneto-optical Faraday effect, first-principles calculation, GaS, GaSe, multilayer

Abstract

Recently, two-dimensional (2D) GaS and GaSe nanosheets were successfully fabricated and the measured electronic, mechanical, and optoelectronic properties are excellent. Here, using the first-principles density functional theory, we investigate the magnetic, optical, and magneto-optical (MO) Kerr and Faraday effects in hole-doped GaS and GaSe multilayers. GaS and GaSe monolayers (MLs) manifest ferromagnetic ground states by introducing even a small amount of hole doping, whereas the magnetism in GaS and GaSe multilayers are significantly different under hole doping. Our results show that ferromagnetic states can be easily established in GaS bilayers and trilayers under proper hole doping, however, most of GaSe multilayers are more favorable to nonmagnetic states. The magnetic moments in GaS multilayers are weakened remarkably with the increasing of thin film thickness and are negligible more than three MLs. This leads to the thickness dependence of MO Kerr and Faraday effects. Furthermore, the MO effects strongly depend on the doping concentration and therefore are electrically controllable by adjusting the number of holes via gate voltage. The substrate effects on the MO properties are also discussed. Combining the unique MO and other interesting physical properties make GaS and GaSe a superior 2D material platform for semiconductor MO and spintronic nanodevices.

1. Introduction

Two-dimensional (2D) layered gallium sulfide (GaS) and gallium selenide (GaSe) have aroused considerable attention due to their excellent optoelectronic, nonlinear optical, and mechanical performances [1–8]. For instance, GaS and GaSe monolayers (MLs) were fabricated to field-effect transistors with high on–off ratio of $10^4$–$10^5$ [1]. Ultrathin GaS and GaSe nanosheets were reported to be good photodetectors with photoresponsivities up to 19.2 and 2.8 AW$^{-1}$, respectively [2, 3]. Bulk GaS and GaSe are materials with great potential for nonlinear optical applications [9, 10]. This can be well inherited into the 2D limit in the sense that a strong optical second-harmonic generation was recently observed in atomic layered GaSe [11]. Moreover, 2D GaS and GaSe were predicted to be more ductile and flexible than graphene and MoS$_2$, because of their smaller in-plane stiffness constants and larger ultimate strains [12].

The study of 2D GaS and GaSe has also been extended to magnetic property. GaS and GaSe MLs exhibit an extraordinary Mexican-hat-like dispersion at the top of the valence band [13–15], akin to the scenarios of InS and InSe [14–18]. The Mexican-hat-like dispersion definitely results in a van Hove singularity in the density of states (DOS). If shifting the Fermi level on the sharp singularity of the DOS (e.g. by hole doping), the electronic instabilities, such as the Stoner-type ferromagnetic phase transition [19–21], can happen due to the reduction of total energy. Though 2D ferromagnets are expected to be useful for the next-generation spintronics, the detection and measurement of magnetization in 2D ferromagnetic GaS and GaSe would be difficult by using traditional means, such as SQUID magnetometer. Fortunately, magneto-optical (MO) Kerr and Faraday effects...
as non-contact (non-destructive) probes have been practically applied in 2D ferromagnetic materials [22]. Moreover, ultrathin films with large MO effects have valuable applications in modern high-density data-storage technology. Following this line, Feng et al [23] and Zhou et al [24] investigated MO Kerr and Faraday effects in hole-doped group-III A metal monochalcogenide MLs (including GaS and GaSe) and blue phosphorene and gray arsenene, respectively.

The thickness, an important aspect of thin films, indubitably influences various physical properties, such as the magnetism [25], mobility [26], and spin-related effective fields [27]. Specifically, the electronic structures of GaS and GaSe significantly depend on the thickness of thin films, exhibiting an evolution of top valence band gradually from the Mexican-hat-like dispersion in ML to the parabolic dispersion in bulk limit [14, 15]. Since the Mexican-hat-like and parabolic dispersions have quite different magnetoresponses in 2D materials [28], it is desired to understand that how the thickness will influence the magnetism and MO effects in hole-doped GaS and GaSe multilayers. In this paper, we detailedly investigate the magnetic, optical, and the MO Kerr and Faraday effects in hole-doped GaS and GaSe multilayers, using the first-principles calculation. It shows that the ferromagnetic ground states can be easily established in GaS bilayers (BLs) and trilayers (TLs) under proper hole doping. However, the magnetic moments are weakened remarkably with the increasing of thin film thickness and can be negligible in the thin films with more than three MLs. In contrast, most of GaSe multilayers prefer the native nonmagnetic states in whole range of hole doping. Thickness-dependent MO Kerr and Faraday effects are found that the MO spectra significantly attenuates with the increasing of thickness. Moreover, the MO effects strongly depend on the doping concentration and therefore are electrically controllable by adjusting the number of holes via gate voltage. Finally, the influences of substrate on the MO effects are studied. We find that the insulating substrates with small refractive indices and smaller lattice constants than GaS and GaSe are beneficial for large MO effects. Our results indicate that GaS and GaSe could be superior 2D material platform for semiconductor MO and spintronic nanodevices by integrating the unique MO and other excellent optoelectronic properties.

2. Computational methods

The calculations in this work are performed by the first-principles density functional theory, implemented in the Vienna ab initio simulation package [29, 30]. The interaction between valence electrons and ionic cores is described by the projected augmented wave method [31], in which the spin–orbit coupling is properly considered. The valence configurations of Ga, S, and Se atoms are $3d^{10}4s^2p^1$, $3s^2p^4$, and $4s^2p^4$, respectively. The exchange-correlation effect is treated with the Perdew et al parameterized generalized-gradient approximation [32]. The conjugate gradient algorithm is used to relax the ionic positions until the force on each ion is less than 0.005 eV Å$^{-1}$. A 12 Å thick vacuum layer is used to avoid the interactions between adjacent atomic layers. The energy cutoff of plane wave is set to be 500 eV. In order to converge precisely the ferromagnetic ground states, energy convergence criterion of $10^{-8}$ eV and $k$-mesh of $31 \times 31 \times 1$ are used for self-consistent field calculation. The vdw-DF-optB88 exchange-correlation functional is adopted to describe the interlayer interactions for BLs and TLs configurations [33, 34]. In order to mimic the hole doping, the number of valence electrons was subtracted and a jellium background with an opposite charge was simultaneously added (keeping the charge neutrality of the unit cell). For each hole doping, the electronic states of GaS and GaSe multilayers are calculated self-consistently, and therefore no rigid band approximation is used. The optical properties are calculated according to the Kubo–Greenwood formula within the linear response theory [35, 36], implemented in the WANNIER90 package [37]. Then, MO spectra can be derived from the optical conductivity [38]. In the thin film limit, the Kerr rotation angle $\theta_K$ and ellipticity $\epsilon_E$ can be written as [39, 40]

$$\theta_K + i \epsilon_E = \frac{2\omega d}{c} \sigma_{xy},$$

where $c$ is the speed of light in vacuum, $\omega$ the frequency of light, $d$ the effective thickness of magnetic layer. $\sigma_{xx}^{\sigma}$ is the diagonal element of optical conductivity tensor of nonmagnetic substrate. Here, we choose SiO$_2$ as the substrate, which has been broadly used to grow 2D GaS and GaSe [1–8, 11]. The dependence of MO effects on different substrates will be discussed later (see figure 5). $\sigma_{xy}$ is the off-diagonal element of optical conductivity tensor of magnetic layer, which is responsible for the origin of the MO effects. For the Faraday effect, the rotation angle $\theta_F$ and ellipticity $\epsilon_{\ell}$ are given by [41],

$$\theta_F + i \epsilon_{\ell} = \frac{\omega d}{2c} (n_+ - n_-),$$

where $n_+$ and $n_-$ are the number of spins up and down, respectively.
with the eigenvalues of the dielectric tensor,
\[ n^2 = 1 + \frac{4\pi i}{\omega}(\sigma_{xx} \pm i\sigma_{xy}). \] (3)

3. Results and discussion

3.1. Crystal and electronic structures

We first briefly introduce the crystal and electronic structures of 2D GaS and GaSe. In a GaS (GaSe) ML, there are two Ga atoms and two S (Se) atoms bonding to a triangular prism along the z axis (D\textsubscript{3h} point group). The calculated lattice constants of GaS and GaSe MLs are 3.65 and 3.82 Å, respectively. Bulk GaS and GaSe usually consist of several MLs, which are stacked perpendicularly to the 2D plane and separated by the van der Waals gap. Depending on the numbers and the arranging patterns of MLs, the crystal structures of bulk GaS and GaSe are manifold, e.g., \( \alpha, \gamma, \beta, \) and \( \delta \) phases [42], as shown in figure 1(a). On the basis of bulk phases, four BLs (figure 1(b)) and three TLs (figure 1(c)) with different arrangements are considered in this work. The B4 and T3 structures have a uniform arrangement of MLs, which cannot be directly extracted from any bulk phases. However, they have the lowest energies comparing to other BLs and TLs, respectively (see table 1).

For GaS and GaSe thin films, the most interesting part in their electronic structures is the top of valence bands, highlighted in figures 2(a) and (e), which exhibit the unique Mexican-hat-like dispersions. This kind of dispersion definitely gives rise to a sharp van Hove singularity of the DOS at the valence band-edge, which is responsible for the Stoner ferromagnetic phase transition under hole doping [23, 24, 28]. The size of the Mexican-hat can be characterized by its width \( b \) and depth \( d \), which presents a thickness dependence that generally shrinks from ML, to BL, and to TL. In addition, a certain stacking pattern can also impact on the profile of valence band top. For example, the B4 (T3) structure (keeping the same arrangement for each ML) is a special one, which presents a larger Mexican-hat comparing to other BLs (TLs), while B1, B2, and B3 (T1 and T2) structures possess the identical profiles reflecting the negligible structural effect between them. For both GaS and

<table>
<thead>
<tr>
<th></th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaS</td>
<td>16.12</td>
<td>16.18</td>
<td>13.71</td>
<td>0.0</td>
<td>35.68</td>
<td>25.37</td>
<td>0.0</td>
</tr>
<tr>
<td>GaSe</td>
<td>14.22</td>
<td>15.13</td>
<td>12.14</td>
<td>0.0</td>
<td>32.28</td>
<td>24.14</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 1. The relative energies (\( \Delta E \)) for the bilayers (B1–B4) and trilayers (T1–T3) of GaS and GaSe. The energies of B4 and T3 are set to be zero. The energy is in the unit of meV.
GaSe, the Mexican-hat has a size sequence of ML > B4 > B3 ≈ B2 > B1 > T3 > T1 ≈ T2. Furthermore, the Mexican-hats of GaS are larger than that of GaSe for ML and each of BL and TL. This can be understood from the relative electronegativities of Ga and S (Se) atoms and the charge transfer between them. Due to the electronegative relation of Se < S, GaS should have larger charges transferring from cation to anion. The transferred electrons will occupy the \( p_z \) orbitals of S atom which dominates the top valence bands. Since the Mexican-hat-like band is responsible for the emergent Stoner-type ferromagnetism under hole doping [23, 24, 28], its size will directly affect the magnetic and MO properties. In contrast to 2D GaS and GaSe, the top valence bands of bulk GaS and GaSe have parabolic dispersions (not shown here), which will not induce ferromagnetism and MO effects under hole doping.

### 3.2. Magnetic and optical properties

Next, we discuss the magnetic and optical properties in hole-doped GaS and GaSe multilayers. Although GaS and GaSe multilayers are nonmagnetic in their native states, the ferromagnetic states possibly emerge under proper hole doping, originating from the reduction of total energy through the Stoner phase transition. Figures 2(b) and (f) plot the magnetic moments of GaS and GaSe multilayers as a function of hole doping concentration \( p \), respectively. It shows that the magnetic moments linearly increase until they reach the maximums \( M_m \) at the critical hole concentrations \( p_m \), then decrease rapidly to zero. The \( M_m \) and \( p_m \) obviously weaken with the increasing of thin film thickness and the trend is almost in accordance with the size sequence of Mexican-hat, i.e., ML > B4 > B3 > B1 ≈ B2 ≈ B3 > T3 > T1 ≈ T2. It should be noted that the magnetic moments in T1 and T2 structures of GaSe TLs are nearly to be zero, because their Mexican-hats are too small and the dispersions around the \( \Gamma \) point are much linear (the dispersions at there are parabolic in other structures). We also calculated the quadlayers of GaS and GaSe and found the magnetic moments are such small that can be omitted. Therefore, the hole doping-induced ferromagnetism cannot happen in GaS and GaSe thin films with the thickness larger than three MLs. To confirm whether the ferromagnetism can take place spontaneously or not, we further calculate the magnetization energy, defined by the energy difference between the nonmagnetic and ferromagnetic states, as a function of \( p \), depicted in figures 2(c) and (g). For GaS and GaSe MLs, the ferromagnetic states can be easily established by introducing a tiny hole [23]. However, the situations in GaS and GaSe multilayers are much different. Although GaS BLs and TLs are nonmagnetic at small doping concentrations (\( p < (0–2) \times 10^{13} \text{cm}^{-2} \)), the ferromagnetic states can still be established at larger hole concentrations. On the contrary, most of GaSe BLs and TLs prefer to nonmagnetic states in the whole doping concentration only except for the B4 structure, which undergoes a magnetic transition from nonmagnetic to ferromagnetic state with the increasing of \( p \). In addition, the magnitude of magnetization energy is reduced considerably with the increasing of layer numbers, indicating that the nonmagnetic states will recover when the thin films are thick enough.
Apart from electronic and magnetic properties, the optical conductivity also shows particular effects by hole doping. Here, we take B1 BL of GaS as an example and the similar results can be obtained in other GaS and GaSe multilayers. The real and imaginary parts of diagonal element ($\sigma_{xx}^{''}$ and $\sigma_{xx}^{'''}$) at different doping levels are plotted in figures 3(a) and (b), respectively, from which one can see that the diagonal element do not change by hole doping because their profiles are totally kept. Nevertheless, the off-diagonal element ($\sigma_{xy}^{'''}$ and $\sigma_{xy}^{''''}$) is essentially altered by hole doping, shown in figures 3(c) and (d). That is, $\sigma_{xy}^{''''}$ equal to zero at $p = 0$ and turn to be finite value when $p > 0$; the magnitudes of $\sigma_{xy}^{''''}$ gradually increase with the increasing of $p$ until the maximums are reached at the critical doping concentrations $p_{c}$, $\sigma_{xy}^{''''}$ suddenly reduce to zero when $p > p_{c}$ due to the vanished magnetic moments.

Physically speaking, the real part of off-diagonal element in the dc limit, i.e.,

$$
\sigma_{xy}^{'}(\omega = 0) = \frac{2}{\pi} \int_{0}^{\infty} \frac{\sigma_{xy}^{'''}(\omega')}{\omega'} d\omega',
$$

is equivalent to the anomalous Hall conductivity (AHC), which can be regarded as an ideal transport probe for itinerant magnetism [43]. The $P$ in above formula denotes the principal part of the integrals. The AHC of GaS and GaSe multilayers as a function of $p$ are plotted in figures 2(d) and (h), which manifest a rough triangle, similar to the behaviors of spin magnetic moment (see figures 2(b) and (f)). Therefore, AHC is available to detect the hole doping-induced magnetism in GaS and GaSe multilayers.

### 3.3. MO Kerr and Faraday effects

As discussed above, the hole doping-induced magnetism in GaS and GaSe multilayers is tunable via the external gate voltage. This gate-tunable 2D ferromagnet is so exciting that has the potential applications for nanospintronics; however, the measurement of magnetism would be extremely difficult by using traditional SQUID magnetometer due to the ultrathin thickness of the samples. Fortunately, modern MO Kerr and Faraday technique as a non-contact probe provides an alternative way to measure the magnetism in atomically thick nanosheet [22].

Figures 3(e)--(h) plot the MO Kerr ($\theta_K$, $\epsilon_K$) and Faraday ($\theta_F$, $\epsilon_F$) spectra for the B1 structure of GaS at different doping levels. Clearly, the MO spectra show similar features to the off-diagonal element of optical conductivity only differing by a negative scaling factor [23], that is,

$$
\theta_K + i\epsilon_K = -\frac{2\omega d}{c\sigma_{xx}^{''}}(\sigma_{xy}^{'} + i\sigma_{xy}^{''}),
$$

$$
\theta_F + i\epsilon_F \simeq -\frac{2\pi d}{c}(\sigma_{xy}^{'''} + i\sigma_{xy}^{''''}),
$$

where $\sigma_{xx}^{''}$ is the imaginary diagonal element of optical conductivity for the substrate. The MO spectra versus hole doping concentration for other GaS and GaSe multilayers are not shown here, because they have similar behaviors to GaS B1 BL.

From figures 2(b) and (f), we learn that the spin magnetic moments significantly decrease with the increasing of thin film thickness. Because of the close relation between magnetic moment and the MO property, it can be reasonably speculated that the MO Kerr and Faraday effects are also thickness-dependent. In order to verify this
The MO Kerr and Faraday spectra of GaS and GaSe multilayers at their critical hole concentrations are plotted in Figure 4. Clearly, the most salient feature is the reduction of spectral heights from MLs, to BLs, and to TLs. The MO effects will eventually disappear when the thickness of thin film is large enough, which essentially results from the evolution of the top valence band from the Mexican-hat-like dispersion to the parabolic dispersion with the increasing of layer numbers [14, 15]. In particular, the MO Kerr and Faraday spectra of GaSe multilayers are negligibly weak comparing to that of ML, which is basically due to the rather small magnetic moments in hole-doped GaSe multilayers. Therefore, the thickness dependence of MO effects in GaSe are more prominent than that in GaS. It should be demonstrated that the MO Kerr and Faraday effects in hole-doped GaS and GaSe multilayers are not only electrically controllable by adjusting the hole numbers via the external gate voltage but also thickness-dependent by growing the multilayer thin films via the molecular beam epitaxy or other experimental techniques.

Finally, we discuss how the MO effects will be affected by the substrate. The lateral (in-plane) strain is an important issue, which originates from the mismatch of lattice constants between the sample and the substrate. We first check the dependence of magnetic moments on such kind of strain, shown in Figures 5(a) and (d). For GaS, the magnetic moments nearly keep a constant in the range of $\varepsilon = -6\%$ to 0% and vanish at larger compressive strains $\varepsilon < -8\%$ and larger tensile strains $\varepsilon > 4\%$. For GaSe, the magnetic moments as a function of the strain present a similar trend except for the accurate platforms. Since the MO effects are strongly dependent on the magnetic moments, the strain can be used to tune the MO effects. From Figures 5(b) and (e), one can see that the Kerr angles of GaS and GaSe MLs can be effectively mediated by adjusting the strain. A substrate with a smaller lattice constant that will generate compressive strain is favorable for large MO effect. Besides the in-plane strain, the dielectric properties of the substrate can directly influence the MO Kerr spectrum in a multilayer film, seen from equation (1). The diagonal element of optical conductivity for a given substrate can be expressed by the refractive index $n$ and the extinction coefficient $\kappa$, i.e., $\sigma_{xx}^{\parallel} = \frac{n^2}{4\epsilon_0}[2\pi n + i(1 - n^2 + \kappa^2)].$ Here, some widely used insulating substrates for growing 2D GaS and GaSe, including SiO$_2$, Al$_2$O$_3$, mica, SiC, and Si, are selected to test their impacts on the MO Kerr effect. Taken the wavelength of the incident light as 589 nm, the complex refractive indices (i.e., $\eta = n + i\kappa$) of above substrates are 1.544, 1.768, 2.450, 2.647, and 3.973 $+ 0.030i$, respectively [44]. The Kerr angles of GaS and GaSe MLs versus different substrates are plotted in Figures 5(c) and (f), from which one can find that the spectral structures are very similar for all of the substrates, while the Kerr angles are inversely proportional to the modulus of $\eta$. Obviously, the largest Kerr angle appears when the SiO$_2$ substrate having the smallest refractive index is adopted. It is undoubtedly that the substrate effects on the MO properties of BLs and TLs resemble that of MLs.

Figure 4. Calculated MO Kerr ($\theta_K, \phi_K$) and Faraday ($\theta_F, \phi_F$) spectra of GaS (a) and GaSe (b) multilayers at the critical hole concentrations $p_{\text{cm}}$, respectively. The results of monolayer (ML) are plotted for the comparison.
4. Summary

In summary, we investigated the magnetic, optical, and MO Kerr and Faraday effects in hole-doped GaS and GaSe multilayers, using the first-principles density functional theory. Under hole doping, the nonzero magnetizations are found in GaS (B1–B4 and T1–T3) and GaSe (B1–B4 and T3) multilayers. The magnetic moments linearly increase up to their maximums and then suddenly reduce to zero, with the increasing of hole concentration. The spontaneous ferromagnetism can only happen in GaS (B1–B4 and T1–T3) and GaSe (B4) multilayers based on the analysis of magnetization energy. For optical conductivity, the diagonal elements cannot be affected by hole doping, i.e., keeping the invariable profile at zero doping, while the off-diagonal elements, being responsible for the emergence of the MO effects, are essentially changed under hole doping. The emergent MO Kerr and Faraday effects in hole-doped GaS and GaSe multilayers are electrically controllable in the sense that they can be effectively tuned by altering the doping concentration via the gate voltage technique. Most importantly, the magnetic moments, optical conductivities (off-diagonal elements), and the MO spectra are thickness-dependent because they significantly weaken with the increasing of layer numbers and will disappear if the thickness is larger than three MLs. Moreover, the substrates with smaller refractive indices and smaller lattice constants than GaS and GaSe are in favor of large MO effects. Our findings would be useful for the applications of 2D MO devices based on GaS and GaSe thin films.

Acknowledgments

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