# Investigation of a +2 oxidation spin state in weakly doped $Cd_{1-x}Ti_xSe$

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Using computational and experimental techniques, we examine the nature of the +2 oxidation of titanium (Ti)-doped CdSe. Through stoichiometry and confirmed through magnetization measurements, the weakly doped  $Cd_{1-x}Ti_xSe$  (x = 0.00043) crystal shows the presence of a robust spin-1 magnetic state of Ti, which is indicative of a +2 oxidation state. Given the obscure nature of the Ti +2 state, we investigate the electronic and magnetic states using density functional theory. Using a generalized gradient approximation with an onsite potential, we determine the electronic structure and magnetic properties for a supercell of CdSe with an ultralow concentration of Ti. We find that, in order to reproduce the magnetic moment of spin-1, an onsite potential of 4–6 eV must be included in the calculation. Furthermore, the electronic structure and density of states show the presence of a Ti-*d* impurity band above the Fermi level and a weakly metallic state for a U = 0 eV. However, the evolution of the electronic properties as a function of the Hubbard U shows that the Ti-*d* drop below the Fermi around 4 eV with the onset of a semiconducting state. The impurity then mixes with the lower valence bands and produces the +2 state for the Ti atom.

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### I. INTRODUCTION

Over the last century, the semiconducting industry has revolutionized both the scientific fields and various industry sectors (i.e., medical technology, finance, and the like) [2] and has presented a large demand for extensive research on properties of the materials that can lead to faster, smaller, and more energy efficient devices. Given the great success of semiconducting materials, research has since extended a focus into understanding how magnetic properties can be embedded into materials to help modify and provide a higher level of efficiency [3].

Titanium is one element that has been used in applications of semiconductors as well for special implants and prostheses for medical uses [4,5]. Titanium is especially interesting because it is a 3d transition metal that typically takes on spin-0 state, leaving it nonmagnetic. This is one reason it makes for good use in substrates like SrTiO<sub>3</sub> [6].

For SrTiO<sub>3</sub>, the titanium matrix is in a Ti<sup>4+</sup> state through stoichiometry, which leaves no valence electrons for the *d* orbitals to create any magnetic moment. However, SrTiO<sub>3</sub> has been shown to take on spin-1/2 magnetic states in the case of oxygen vacancies [7,8], where the lack of oxygen in the matrix induces a Ti<sup>3+</sup> state and spin-1/2 magnetic moment. This is typically randomized throughout the substrate, producing weak magnetism. Additionally, titanium's propensity to obtain a nonmagnetic state [9,10] is likely one reason for the low solubility limit for Ti alloys [11].

The investigation of small magnetic impurities in nonmagnetic semiconductors has been studied a great deal for decades within the context of diluted magnetic semiconductors [12–17], where these materials provide a venue for these types of interactions. Many of these studies focused on transition-metal alloys consisting of semiconducting materials doped with select transition-metal atoms [13,15,18–20]. While there are many semiconductors of interest, in this study, we focus on cadmium selenide (CdSe) [21,22].

CdSe is a focus of intense research due to its potential use in quantum technologies, including quantum information storage and computation [23]. The ability of CdSe to exhibit semiconductor properties suggests the material has potential in applications like quantum dots, solar cells, and even immunofluorescence labeling biotechnology [21,23,24].

The doping effects of CdSe with transition-metal elements have demonstrated a distinct shift in the electronic properties and the introduction of magnetic behavior [2,25-28]. To understand how efficient the doped semiconductor is for use, a great deal of both theoretical and experimental studies are being conducted to observe properties such as the magnetic moment and gap energy. Changes in these properties stem from the induced magnetic state of the dopant. From stoichiometry, Cd must hold a 2+ oxidation state. Therefore, a dopant replacing Cd will take on a 2+ state. Consequently, if CdSe is doped with Ti, the Ti will be "forced" into either a spin-1 state assuming the  $T_d$  crystal-field symmetry [29], a fairly unusual magnetic state for Ti, or a spin-0 state.

In this study, we examine the stoichiometric nature of the low-doped concentration of Ti in CdSe. We present magnetization measurements that clearly demonstrate a S = 1 state for Ti, indicating an obscure 2+ oxidation state for Ti. As mentioned above, while this is expected through stoichiometry, Ti rarely forms a spin-1 state. Therefore, to better understand this obscure state, we explore the electronic and magnetic properties of  $Cd_{1-x}Ti_x$ Se with a low concentration of Ti using density functional theory. An analysis of the electronic structure calculations reveals a strong Hubbard U potential on the Ti atom in the CdSe matrix, which produces the 2+ oxidation state and induces the semiconducting state.

There have been a few studies on Ti-doped CdSe. In 1973, Böttcher and Dziesiaty performed early electron paramagnetic



FIG. 1. (a) Top view of the  $Cd_{1-x}Ti_xSe$  mother compound with Ti dopant embedded within the CdSe matrix (Ti not visible from above). (b) Side view of  $Cd_{1-x}Ti_xSe$  mother compound with Ti dopant embedded within the CdSe matrix. (c) Illustration of the tetrahedron around Ti. The changes in bond lengths and bond angles are detailed in Table I.

resonance (EPR) measurements on a weakly Ti-doped sample of CdSe. In this study, they show that the system exhibits a very small anisotropy [1]. In 2017, El Amine Monir *et al.* performed density functional calculations on 25%, 50%, and 75% Ti-doped CdSe [30]. However, this study does not examine the weakly doped case, which is problematic as CdSe has a low solubility limit with Ti and is not likely to reach a doping level that high.

### II. EXPERIMENTAL AND COMPUTATIONAL METHODOLOGY

 $Cd_{1-x}Ti_xSe$  crystals were grown using the modified vertical Bridgman technique using  $\leq 2\%$  nominal Ti concentration due to the low solubility. The crystallographic  $\hat{c}$  axis was determined using the x-ray Laue method.

TABLE I. Bond lengths and angles for Cd- and Ti-centered tetrahedrons.

| Bond length (Å)            | Cd-Se    | Ti-Se    |
|----------------------------|----------|----------|
| $r_1$                      | 2.633    | 2.525    |
| $r_2$                      | 2.634    | 2.534    |
| <i>r</i> <sub>3</sub>      | 2.633    | 2.526    |
| $r_4$                      | 2.633    | 2.525    |
| Bond angles (degrees)      | Se-Cd-Se | Se-Ti-Se |
| $\theta_{1 \rightarrow 2}$ | 109.4    | 107.9    |
| $\theta_{1 \rightarrow 3}$ | 109.5    | 111.0    |
| $\theta_{1 \rightarrow 4}$ | 109.5    | 110.9    |
| $\theta_{2 \rightarrow 3}$ | 109.4    | 108.0    |
| $\theta_{2 \to 4}$         | 109.4    | 107.9    |
| $\theta_{3 \rightarrow 4}$ | 109.5    | 111.0    |



FIG. 2. Magnetization as a function of temperature with  $H \perp C$  for various applied fields for  $Cd_{1-x}Ti_xSe$ . Note the increasing saturation of the paramagnetic spins at low temperatures for the 7 T data in the inset. The lines are a guide to the eye.

Magnetization measurements were performed on a single crystalline sample of  $Cd_{1-x}Ti_xSe$  with x = 0.00041 using a Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer. Measurements were conducted at temperatures between 2 and 400 K and in fields up to 7 T parallel and perpendicular to the *c* axis. The diamagnetic contribution due to the host CdSe has been subtracted from the data. The low doping concentration is due to the extremely low solubility limit of Ti in CdSe [29].

The *ab initio* calculations are performed based on the density functional theory using the atomistic orbital approach implemented in Quantum Atomistix Toolkit (QuantumATK) [31–33]. Calculations are carried out within the spin-polarized generalized gradient approximation (SGGA) to the exchange-correlation functional (PBE) with a variable onsite potential. The Hubbard U was used to ensure a semiconducting ground state.

To get the 0.04% concentration would have required a supercell with  $10^4$  atoms, which would be too computationally expensive. Therefore, to obtain a low enough concentration of Ti while optimizing the computational cost, we focused on a 108-atom supercell of CdSe in the wurtzite configuration ( $P6_3mc$ ) and replaced one Cd atom with Ti, which provided only an  $\approx 2\%$  concentration. While this is higher than the measured concentration of 0.04%, the Ti atom is



FIG. 3. Magnetization as a function of applied magnetic field for  $Cd_{1-x}Ti_xSe$  with  $H \parallel C$  (blue upside-down triangles) and  $H \perp C$  (red triangles) for variable temperatures showing a very small anisotropy, which is consistent with EPR measurements from Ref. [1]. The lines are a guide to the eye.

isolated enough that its surrounding environment should be very similar. Figure 1(c) shows the tetrahedron around the

Ti-substituted atom. In Table I, we show the difference in bond lengths and bond angles for both Cd-centered and Ti-centered tetrahedrons. This illustrates the structural distortions in the crystal lattice due to the presence of Ti.

Starting with a 108-atom supercell of CdSe, one Cd atom was replaced with Ti. The lattice was relaxed to a 0.01 Å/eV tolerance. To examine electronic and magnetic properties, we calculated the electronic band structure, density of states, magnetic moment, and optical properties using a  $(3 \times 3 \times 3)k$ -point sampling given the size of the supercell. Test calculations at a higher *k*-point sampling showed no detectable difference in the electronic structure and density of states.

GGA + U calculations are known to underestimate that band gap in the electronic structure due to a low-lying electronic band above the Fermi level. Therefore, GGA calculations typically underestimate the band gap to be around 0.5 eV [34,35], even though the miscellaneous band has little to no weight in the density of states, which is why hybrid functionals are typically used. However, given the large supercell of CdSe, we chose to model the electronic and magnetic behavior with SGGA + U calculations due to computational restrictions. Additionally, since we are examining the magnetic states of Ti-doped CdSe, we mainly care about the valence states as opposed to the precision of the conduction states.

#### **III. MAGNETIZATION MEASUREMENTS**

Magnetization versus temperature data for our  $Cd_{1-x}Ti_xSe$  crystal is shown in Fig. 2 for H = 0.1, 1, and 7 T aligned perpendicular to the *C* axis. The lines are a guide to the eye. At high temperatures, the magnetization above 50 K is small due to the combined effects of a low Ti concentration and increasingly larger thermal effects. In contrast, the magnetization grows rapidly at low temperatures. On closer examination below 5 K (see inset), the magnetization shows signs of saturation in the 7 T data. In the lower 1 and 0.1 T



FIG. 4. Brillouin fits to the  $Cd_{1-x}Ti_xSe$  magnetization data for temperatures between 2 and 20 K using fit parameters of S = 1/2, 1, and 3/2. The best fit is obtained for values of S = 1 and x = 0.00041.



FIG. 5. The electronic band structure and density of states for (a) CdSe and Ti-doped CdSe with (b) U = 0, (c) 2, (d) 4, and (e) 6 eV. The density of states has also been broken into the partial (orbital components) and local (atomic components) density of states.

applied fields, there is no indication that the magnetization is approaching saturation. This is consistent with the Ti ions exhibiting paramagnetic behavior.

Figure 3 shows the magnetization data for  $Cd_{1-x}Ti_xSe$ (x = 0.00041) with  $H \perp C$  (shown by red triangles) and  $H \parallel C$  (shown by blue upside down triangles), which demonstrates the relatively weak anisotropy exhibited by this system.

To explore this further, we examine the magnetization as a function of applied field at temperatures below 20 K. The magnetization data taken at 2, 4.2, 5, 10, and 20 K are shown in Figs. 4(a)-4(c) as solid circles. At 20 K, the magnetization increases approximately linearly up to 7 T with no indication of approaching saturation. At 2 K, the magnetization departs from the linear behavior and approaches saturation by 7 T. This behavior is again typical of the paramagnetic behavior of the Ti ions in our Cd<sub>1-x</sub>Ti<sub>x</sub>Se crystal. The 2 K data were fit using a Brillouin function [36,37] for S = 1/2, 1, and 3/2, shown as solid blue lines in Figs. 4(a)–4(c), respectively. As can be seen, the 2 K data are reasonably fit using the Brillouin function for values of S = 1/2 and 1. The fit for S = 3/2 is visibly the poorest fit of the three, giving an initial indication that the Ti ions are not likely in the S = 3/2 state. From these Brillouin fits, we also begin to narrow the range of the concentration *x* in our Cd<sub>1-x</sub>Ti<sub>x</sub>Se crystal to fall between x = 0.000 86 and 0.000 27.

As the temperature is raised from 2 to 20 K at 7 T, the additional thermal energy allows the moments to deviate from near the saturated value and the measured magnetization decreases. This can be seen in the magnetization at 7 T as the temperature is increased to 4.2, 5, 10, and 20 K in Figs. 4(a)-4(c). Keeping the values for x obtained from the Brillouin fit at 2 K for each value of S, additional Brillouin function calculations



FIG. 6. (a) Plot of the gap energy of  $Cd_{0.98}Ti_{0.02}Se$  as a function of Hubbard U at 0, 2, 4, and 6. The system reaches a semiconducting state as the Hubbard U about the Ti atom increases. (b) Plot of the magnetic moment of  $Cd_{1-x}$  Ti<sub>x</sub>Se as a function of Hubbard U consistent with the gap energy plot.

are plotted as solid lines and compared with the measured magnetization at higher temperatures. As shown in Fig. 4(b), the Brillouin calculations for S = 1 continue to describe the measured magnetization over this full range of temperatures. In contrast, there is clear disagreement between the measured and calculated values at higher temperatures for S = 1/2 and 3/2. From this, we can conclude that the Ti ions in Cd<sub>1-x</sub>Ti<sub>x</sub>Se are in the S = 1 state, and our Cd<sub>1-x</sub>Ti<sub>x</sub>Se crystal has a Ti concentration of x = 0.00041.

#### **IV. DENSITY FUNCTIONAL CALCULATIONS**

To provide further context to the experimental results, we performed density functional calculations on a CdSe with a very low concentration of Ti. To analyze these calculations, we determined the electronic band structure, density of state, and magnetic moment as onsite Hubbard U potential functions.

Figure 5(a) provides all of the electronic band structure and density of states results for CdSe and  $Cd_{0.98}Ti_{0.02}Se$  with various U values [Figs. 5(b)–5(e) for 0, 2, 4, and 6 eV].



FIG. 7. The band structure with projected orbital contributions for CdSe (left panel) and Ti-doped CdSe (right panel) with U = 6 eV. The projected orbital contributions are red (Se *p*-orbitals), blue (Cd *p* orbitals, green (Cd *d* orbitals), and purple (Ti *d* orbitals). The Se *p*-orbital contribution for the Ti-doped system has been removed because it is the same as the undoped CdSe system. The lower panel shows only the Ti *d* orbitals in the valence band, which consists only of contributions from the t2g orbitals (mainly the  $d_{xy}$  and  $d_{yz}$  orbitals.)

In Fig. 5(a), the band gap for CdSe is underestimated due to the presence of a single Se band, which is consistent in GGA calculations. However, an examination of the density of states reveals the standard band gap of about 1.8 eV, consistent with previous literature. [28,38,39]. As shown in Fig. 5(b), the addition of the single Ti atom dramatically shifts the band structure into a weakly metallic state. However, by introducing a Hubbard U potential to the Ti 3dorbitals, the bands shift upward and make the system semiconducting at around U = 3 or 4 eV [Figs. 5(c)-5(e)]. This metal-to-semiconducting transition is also shown in the density of states, where it is clear that the presence of the Ti atoms has a metallic response around the Fermi level for the Ti local density of states (LDOS). Furthermore, you can observe a distinct response in the LDOS of the nearest-neighbor atoms as the Ti is clearly influencing the environment around it.

We examined the magnetic moment and benchmarked the material to undoped CdSe to guarantee that we are in the proper ground state. By stoichiometric analysis, the Ti should be in a 2+ state, which could be either a spin S = 0 (low spin) or S = 1 (high spin) state. Figure 6(a) shows the magnetic

moment as a function of Hubbard U. Here, it is clear that at a U = 0eV, the Ti atom is in a S = 1/2 state, which contradicts the stoichiometric analysis. However, Figure 6(b) shows this is the metallic state. Therefore, as the Hubbard U is increased, not only does the energy form and produce a semiconductor, but the magnetic moment on the Ti atom becomes more localized and increases into the S = 1 range. This helps to confirm that the measured S = 1 response of magnetization measurements.

### V. DISCUSSION AND CONCLUSION

The challenge with this system is titanium does not typically take on spin-1 state. The Ti atom has four valance electrons and, in most lattice structures, will produce a 4+ or a 3+ state carrying no spin or a spin-1/2, respectively, due to titanium's affinity towards the formation of tetrahedral lattice structures [29,40]. However, in the CdSe system, replacing Cd with Ti would put in a 2+ state, resulting in either no spin or a spin-1 state, which is unusual for Ti. This is due to the Ti being forced into a distorted octahedral crystal field.

To examine this further, we show the projected orbital contributions of CdSe and Ti-doped CdSe in Fig. 7. Here, the addition of the Ti atom into the CdSe matrix introduces two degenerate *d* orbitals below the Fermi level (specifically,  $d_{xy}$  and  $d_{yz}$  orbitals). A normal octahedral structure would have three degenerate orbitals. However, due to the crystal structure of the system and the two-sublattice nature of the honeycomb lattice, two of the *d* orbitals are slightly lower in energy (hence a distorted octahedral crystal field.) Due to the degenerate

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energies of the orbitals, the two valence electrons for Ti will form the S = 1 state.

As shown above, both the magnetization data and density functional calculations clearly demonstrate that Ti is in the spin-1 state. While this is not surprising from the stoichiometric standpoint, the tendency for Ti to have such an obscure state is relevant for understanding other physical aspects of the system. For example, in other doped CdSe systems, the solubility limit is much higher [27,41]. However, for the Ti compound, it is quite low. Therefore, based on this study, it is implied that there is a distinct connection between the preferred oxidation state and the solubility limit, especially in the case of titanium.

Additionally, the density functional calculations show that in order for the Ti-doped CdSe system to obtain a semiconducting state, the Ti must be in the spin-1 oxidation state  $(Ti^{2+})$ . This means that the Ti atom is forced to have a strong onsite potential, which makes the titanium hold its valence electrons tighter. If the Ti increases its oxidation state, then the system is pushed towards a metallic state as the valence electrons of the selenium would be pushed toward the Fermi level.

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