Research Article

Half-Metallic Ferromagnetism in Chalcopyrite 
(AlGaMn)P₂ Alloys

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1. Introduction

Diluted magnetic semiconductor (DMS) materials have become a great interest because the charge from the s and p electrons of the nonmagnetic semiconductor and the spin from the magnetic dopant can be used in spintronics devices [1–6]. Ferromagnetism has been reported in various semiconductor groups including II-VI [3, 7], III-V [3, 8], and II-IV-V₂ [9]. However, to date, the opportunities of DMSs applications have been limited due to the low solubility of magnetic ions in nonmagnetic semiconductor hosts. Thus it is one of the primary challenges to create the ferromagnetic (FM) semiconductors due to the difficulty in the spin-injection into the semiconductor to form DMS at room temperature or above room temperature.

When FM metals are used as spin injectors, the polarization in the semiconductor tends to be quickly lost via spin-flip scattering. It has been reported that the Mn-doped chalcopyrite such as ZnSnAs₂ [9] and ZnGeP₂ [10] shows FM ordering at 320 and 312 K, respectively. A newly synthesized MnGeP₂ ternary compound has been reported as a semiconductor whose crystal structure is chalcopyrite. It has been reported that MnGeP₂ exhibits ferromagnetism with \( T_C = 320 \) K and a magnetic moment per Mn at 5 K of 2.58 \( \mu_B \), and an indirect energy gap of 0.24 eV.

Overberg and coworkers have investigated ion implantation of Cr or Mn at concentrations of 1–5 at.% in Al₀ₓGa₁₋ₓP \( (x = 0.24, 0.38) \) eplayers grown by gas source molecular beam epitaxy [11, 12]. The FM-like ordering has been observed above 100 K for Cr and 300 K for Mn in AlGaP. The Mn dopant appears to be a more promising choice than Cr for high temperature ferromagnetism in AlGaP. AIP is unstable in air and oxidizes rapidly. However, ternary AlGaP material is used in the device structures. We see it can enhance the Curie temperature while maintaining material stability. Other recent experiments for (Ga,Mn)P show ferromagnetism above 300 K [13–15]. The Curie temperature is strongly influenced by the carrier density and type in the material with highly \( p \)-type samples showing much higher values than \( n \)-type or undoped samples. Finally, it can be found that the Curie temperature increases with Mn concentration.

In the paper, the electronic and magnetic properties of (Al,Mn)-codoped to fabricate GaP-based DMS have been studied by using first-principle calculations. In the system of AlGaP, Mn, we observed the FM ordering with high magnetic moment (\( ~3.8 \mu_B/Mn \)). We predicted that AlGaP...
ternary compound can have a character of chalcopyrite semiconductor with a direct band gap. Chalcopyrites, which are genealogically related to the more familiar tetrahedrally coordinated zinc-blende materials, are a class of semiconductors recognized as promising materials for nonlinear optical applications.

2. Computational Methodology

The electronic structure and magnetic properties on the (Al,Mn)-codoped GaP semiconductor which consists of a supercell of 64 atoms have been investigated. We checked three doping levels of 6.25%, 9.375%, and 12.5% of Mn atoms, respectively. The first-principles simulations were performed using the full-potential linear muffin-tin orbital (FPLMTO) method [16] based on density functional theory (DFT). All calculations were performed within the generalized gradient approximation (GGA) with the exchange-correlation functional proposed by Perdew-Burke-Ernzerhof scheme [17]. The muffin-tin radii of Mn (or Al, Ga) and P were chosen to be 2.4 and 1.9 a.u., respectively, with the plane-wave energy cutoff by 596.6 eV. The convergence tests of the total energy with respect to the plane-wave energy cutoff and \( k \)-point sampling have been carefully examined.

The LMTO basis set and charge density were expanded in terms of the spherical harmonics up to \( l = 6 \) inside each muffin-tin sphere. The LMTO basis functions in the valence energy region were chosen as 4s and 3d for Mn, and 4s, 4p, and 3d for Ga. The basis function of Mn (or Al) for the 4s (or 3s), 4p (or 3p), and 3d is generated with cutoff energy of 159.12 eV, 232.56 eV, and 340.0 eV, respectively. The valence electrons were not assumed to have the spin-orbital coupling but generated the self-consistent supercell potential by considering the scalar relativistic effects. The atomic potentials were approximated by spherically symmetric potential; however the full charge density including all nonspherical terms was evaluated in Fourier series in the interstitial region on the FPLMTO method. The charge density is determined self-consistently by using a gamma-centered \( 4 \times 4 \times 4 \) grid in the Brillouin zone. Using 64 \( k \) points of \( 4 \times 4 \times 4 \) grid insured that the total energies and the magnetic moments were converged on a better 10 meV/cell and 0.01 \( \mu_B \)/atom scale, respectively.

3. Results and Discussion

For the AlP, GaP, and pure AlGaP\(_2\) systems, we considered the atomic relaxations for the positions of the structures. The atomic geometry and positions of the structures were fully relaxed until the force between atoms was less than 1.0 mRy/Bohr. However, the distortions of near host atoms by substituting Mn dopant in the AlGaP\(_2\) bulk were neglected. We found the equilibrium lattice parameters for the chalcopyrite structure from first-principles calculations. The equilibrium lattice parameters are \( a = 5.726 \text{Å} \) and \( c = 11.452 \text{Å} \) for GaP; \( a = 5.648 \text{Å} \) and \( c = 11.296 \text{Å} \) for AlP. For AlGaP\(_2\), they are \( a = 5.685 \text{Å}, c = 11.222 \text{Å}, \) and \( c/a = 1.974 \). In the case of GaP and AlP systems, we performed a minimization of total energy for the supercell volume keeping the constant \( c/a \) ratio (=2.0). For the AlGaP\(_2\) system, we considered the structural relaxation for each of \( a \) and \( c \)-axis. The calculated parameters for GaP and AlP can be compared with that of the zinc-blende structure. The experimental values are \( a = 5.451 \text{Å} \) and \( 5.450 \text{Å} \) for GaP [18, 19] and AlP [18], respectively. The chalcopyrite GaP, AlGaP\(_2\), and AlP structures exhibit the semiconducting character with energy gaps of 0.276 eV, 1.241 eV, and 1.679 eV, respectively. We can see a downward bowing of the lattice parameter with respect to the Al concentration increases in the Al\(_{1-x}\)Ga\(_x\)P\(_2\) system (\( x = 0.0, 0.25, 0.75, \) and 1.0), while the band gap increases from 0.276 eV to 1.679 eV. The band gap is smaller than the experimental value [20]. In general, the magnitude of band gap calculated using the GGA or LDA (local density approximation) is less than half of the value obtained in the experiment. The chalcopyrite AlGaP\(_2\) indicates a semiconducting character with direct band gap (not to be seen in the figure). The tetrahedral chalcopyrite structure was displayed in Figure 1. The lattice parameters for each crystalline and the energy gap were listed in Table 1.

We found that the Al(Ga,Mn)P\(_2\) is more energetically favorable than the (Al,Mn)GaP\(_2\) (Ga-rich). However, the difference in the substitution energies between both systems is very small. The substitution energy is \(-346.5 \text{meV}\)
Figure 2: DOS for Al, Ga, P, and Mn sites of 3.125% Mn-doped AlGaP$_2$ in the FM state. The Fermi level is set to zero.
Figure 3: DOS for Al, Ga, P, and Mn sites of Ga-rich \( (\text{Al}_{1-y}\text{Mn}_y)\text{GaP}_2 \) with \( y = 0.0625 \), 0.09375, and 0.125 in the FM state. The Fermi level is set to zero.
and $-282.2$ meV for Al(Ga_{3.0}Mn_{1.0})P_2 and (Al_{3.0}Mn_{1.0})GaP_2, respectively. The substitution energy was defined as

$$E_{\text{sub}} = E(\text{AlGaP}_2; \text{Mn}) - E(\text{AlGaP}_2)$$

where $E(\text{AlGaP}_2; \text{Mn})$ and $E(\text{AlGaP}_2)$ are the total energies of (AlGaMn)P_2 and the pure AlGaP_2, respectively. $\mu_{\text{Mn}}$, $\mu_{\text{Al}}$, $\mu_{\text{Ga}}$, and $\mu_{\text{P}}$ are the atom chemical potentials of Mn, Al, Ga, and P atoms, respectively. $\mu_{\text{Al}} = E(\text{AlP}(\text{bulk})) - E(\text{P}(\text{bulk}))$ and $\mu_{\text{Ga}} = E(\text{GaP}(\text{bulk})) - E(\text{P}(\text{bulk}))$. Under Al-rich conditions, $\mu_{\text{Mn}} = E(\text{MnP}(\text{bulk})) - E(\text{AlP}(\text{bulk}))) + E(\text{Al}(\text{bulk}))$ and $\mu_{\text{P}} = E(\text{AlP}(\text{bulk})) - E(\text{Al}(\text{bulk})))$; and under Ga-rich conditions, $\mu_{\text{Mn}} = E(\text{MnP}(\text{bulk})) - E(\text{GaP}(\text{bulk}))) + E(\text{Ga}(\text{bulk}))$ and $\mu_{\text{P}} = E(\text{AlP}(\text{bulk})) - E(\text{Ga}(\text{bulk})))$. The chemical potentials depend on the experimental conditions under which the material is grown. In order to determine these quantities, we invoke the relationship $\mu_{\text{Al}} + \mu_{\text{Ga}} + 2\mu_{\text{P}} = \mu_{\text{AlGaP}_2}$, assuming these species are in thermal equilibrium with AlGaP_2. The atomic chemical potential for Mn is assumed to be determined by equilibrium with bulk MnP which is the FM phase with a Neel temperature of 291 K [20].

For Al(Ga_{1-y}Mn_{y})P_2 (Al-rich) and (Al_{1-y}Mn_{y})GaP_2 (Ga-rich) for $y = 0.03125$, 0.0625, (or 0.09375), and

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**Figure 4:** Band structures for Ga-rich $(\text{Al}_{1-y}\text{Mn}_y)\text{GaP}_2$ of (a) and (b) and Al-rich Al$(\text{Ga}_{1-y}\text{Mn}_y)\text{P}_2$ of (c) and (d) with $y = 0.0625$ and 0.125 in the FM state. The Fermi level is set to zero.
0.125, the electronic structure and magnetic properties were investigated. Figure 2 shows the density of states (DOS) for Al(Ga$_{3-y}$Mn$_y$)P$_2$ and (Al$_{3}$Mn$_y$)GaP$_2$ with the FM state at $y = 0.03125$. Figure 3 shows the DOS for (Al$_{3}$Mn$_y$)GaP$_2$ (Ga-rich) with the FM state at $y = 0.0625$, 0.09375, and 0.125. The band structures for the systems of Ga-rich and Al-rich with the Mn concentrations of 6.25 and 12.5% are shown in Figure 4. The FM state is more energetically favorable than the nonmagnetic or antiferromagnetic (AFM) state. The difference in total energy between the FM and AFM states ($E_{\text{total}}(\text{FM}) - E_{\text{total}}(\text{AFM})$) is $-21.4\text{ meV}$ in the Mn concentration of 3.125%. In the case of (Al$_{3}$Mn$_{1.0}$)GaP$_2$ (it corresponds to $y = 0.0625$), the nearest neighboring four surrounding P atoms which formed the MnP$_4$ tetrahedron are aligned positively with magnetic moments of 0.05 $\mu_B$ per P atom. For the nearest neighboring Al or Ga atoms, it is aligned negatively with magnetic moment of $-0.02\mu_B$ per Al or Ga atom. Even though it increases up to a Mn concentration of 12.5%, the Mn dopant is maintained to the FM state with high magnetic moment. These results were listed in the Table 2.

We could observe the perturbation of the valence band by dopant Mn in the host AlGaP$_2$ bands. The minority states exhibit the downward shift in energy by about 0.5 eV in comparison with undoped AlGaP$_2$, while the majority states exhibit the upward shift in energy by about 0.5 eV. A localized state is formed just at the Fermi level ($E_F$). The band of majority state on the $E_F$ occupies Al-3p and Ga-4p, and P-3p electrons mainly. These majority p states make a result of strong hybridization between the P-3p (or Al-3p, or Ga-4p) and Mn-3d ($t_2$, $d_{x^2-y^2}$) bands, or Mn-3d ($e$, $d_{x^2-y^2}$) bands. The P-3s state is localized below $E_F - 10.5$ eV. The partially filled Mn e-band lies on the $E_F$ (mainly majority states), while the $t_2$-band falls into the valence band by $E_F - 2.5$ eV. In particular, a strong interaction between Mn-3d and P-3p occurs due to the carrier accumulation between the Mn and neighboring P atoms just on the $E_F$. Hence the partially filled p band (mainly P-3p electrons) contributes to the ferromagnetism with high magnetic moment. These configurations provide us with clues to elucidate the mechanism of the carrier (holes)-mediated ferromagnetism in the DMS (Al$_{3}$Mn$_{y}$)GaP$_2$.

The substituted system of Al or Ga by Mn atom shows the half-metallic character due to downward shift of the host Al, Ga, and P minority bands. From Figures 3 and 4, we can find that the half-metallic behavior retains as Mn concentration increases. The magnetic moment is nearly constant as Mn concentration increases. The direct Mn 3d-3d correlation between Mn atoms may be small because the variance of magnetic moment with respect to the Mn concentration is not changed nearly. The Mn-P bond in chalcopyrite (AlGaMn)P$_2$ is largely covalent because of the strong hybridization between the Mn-3d and P-3p states; when it occurs, the substitution of Al or Ga by Mn, the Mn dopant with P atoms, forms the P-Mn-P bond within the MnP$_4$ tetrahedron.

### 4. Concluding Remarks

In conclusion, the AlGaP$_2$ chalcopyrite compound is a $p$-type semiconductor with a band gap of 1.24 eV. For Mn-doped AlGaP$_2$, the FM state is the most energetically favorable as compared to the other states. We have observed that this system exhibits the FM and half-metallic ground state. It illustrates the stability of FM state with respect to the Mn-doping concentration. The Mn magnetic moment is constant nearly with $3.8\mu_B$/Mn as Mn doping concentration increases. The FM ordering of the dopant Mn and four neighboring P atoms is produced by strong p-d hybridization. Even though it is necessary to investigate more in the DMS limit, we expect it to be an application of useful DMS in the spintronics.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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### References


