

Room-Temperature Ferromagnetism in Mn-Doped Semiconducting CdGeP₂

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The chalcopirite CdGeP₂ doped with Mn has been recently found to exhibit room-temperature ferromagnetism. In addition to the substitution of Mn for Cd, the creation of... in

formation energy of α . Since the formation energies are conventionally defined with respect to the elemental solid(s), we prepare μ_α^a as the sum of a component μ_α^s of the element in its most common occurring structure μ_α^s , and an effective chemical potential μ_α , i.e., $\mu_\alpha^a = \mu_\alpha^s + \mu_\alpha$. Here μ_α^s for P, Ge, Mn, and Cd are the total energies calculated for the full optimized elemental solid in the observed crystal structure [14]. If $\Delta H_f(\text{CdGeP}_2)$ is the formation energy of CdGeP_2 , then μ_{Cd} and μ_{Ge} are determined by

$$\mu_{\text{Cd}} + \mu_{\text{Ge}} + 2\mu_{\text{P}} \leq \Delta H_f(\text{CdGeP}_2). \quad (2)$$

Furthermore, $\mu_{\text{Cd}} \leq 0$; $\mu_{\text{Ge}} \leq 0$, because otherwise the elemental solid will precipitate. The presence of oxygen in the binary phase, however, further restricts the values of μ_{Cd} and μ_{Ge} : One must solve Eq. (2) along with the constraints placed by the formation energies $\Delta H_f(\text{Cd}_3\text{P}_2)$ and $\Delta H_f(\text{GeP})$ of Cd_3P_2 and GeP :

$$3\mu_{\text{Cd}} + 2\mu_{\text{P}} \leq \Delta H_f(\text{Cd}_3\text{P}_2), \quad (3)$$

$$\mu_{\text{Ge}} + \mu_{\text{P}} \leq \Delta H_f(\text{GeP}), \quad (4)$$

to find the allowed range for μ_{Cd} and μ_{Ge} in CdGeP_2 . The electron ionization potential forming a point defect joins the Fermi level to the formation energy increase by $q\epsilon_f$, where ϵ_f is the Fermi energy which varies from 0 eV at the valence band maximum (VBM) of the host material to the band gap of the host. Equation (2)–(4) are solved using the experimental values [15,16] of the formation energies for the binary phase Cd_3P_2 (−1.2 eV) and GeP (−0.3 eV), while a value of −1.5 eV, in the same range as other chalcogenides [17], is used for CdGeP_2 .

The allowed range of chemical potential μ_{Cd} and μ_{Ge} for CdGeP_2 and the binaries Cd_3P_2 and GeP are given in Fig. 1. There are three distinct chemical potential domains where CdGeP_2 can exist: point A: Cd rich, Ge poor;

point B: Cd rich, Ge-rich; and point C: Cd poor, Ge rich. Figure 2 shows the formation energies of the intrinsic point defects Ge_{Cd} , V_{Cd} , and V_{Ge} as well as the substitutional defects Mn_{Ge} and Mn_{Cd} at the chemical potentials A, B, and C of Fig. 1 as a function of the Fermi energy. The vertical dashed line denotes the generalized gradient approximation (GGA) gap which is indeed indicated by the experimental 1.72 eV gap. Transition points between charge states are indicated by solid circles. The defects can

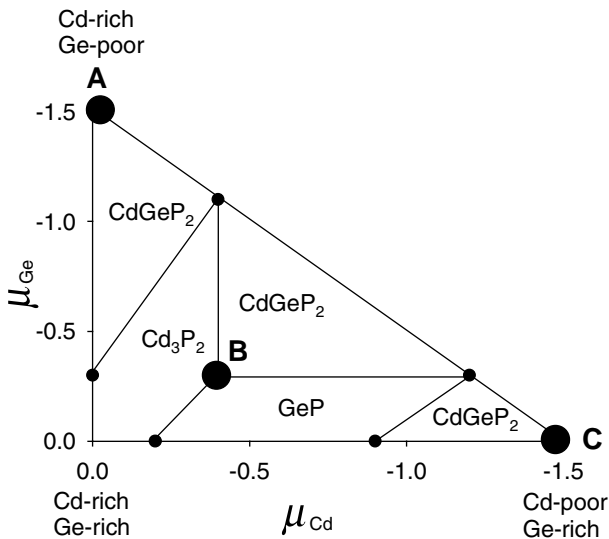


FIG. 1. The range of Cd and Ge chemical potential where CdGeP_2 , GeP , and Cd_3P_2 are stable.

in the condition has no hole and cannot promote an antiferromagnetic (Ge-on-Cd) interface with high formation energy, and would therefore not have appreciable concentration.

Having identified the hole-producing center has confirmed field FM, we need to examine the predicted solubility of interstitial Mn. Our calculated formation energies for $\text{CdGeP}_2:\text{Mn}$ and similar calculations for $\text{GaAs}:\text{Mn}$ have consistently lower values (for the appropriate chemical potential) in the former case, predicting higher Mn solubility: The lowest formation energy of interstitial Ga atoms in GaAs is 1.0 eV (under Mn-rich, Ga-poor conditions). In contrast, even in the former case scenario, we find a

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