Room-Temperature Ferromagnetism in Mn-Doped Semiconducting CdGeP$_2$

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The chalcopyrite CdGeP$_2$ doped with Mn have been recently found to exhibit room-temperature ferromagnetism. Isovalent substitution of the Cd site is expected, however, to create ... .m. ..., m. in

atom is removed. μ_α^a is the absolute value of the chemical potential of atom α. Since the formation energies are conventionally defined with respect to the elemental solid(s), we express μ_α^a as the sum of a component due to the element in its most commonly occurring structure μ_α^s, and an excess 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 evaluated for the fully optimized elemental solids in the observed crystal structures [14]. If $\Delta H_f(CdGeP_2)$ is the formation energy of $CdGeP_2$, then μ_{Cd} and μ_{Ge} are determined by

$$\mu_{Cd} + \mu_{Ge} + 2\mu_P \leq \Delta H_f(CdGeP_2). \qquad (2)$$

Furthermore, $\mu_{Cd} \leq 0$; $\mu_{Ge} \leq 0$, because otherwise the elemental solids will precipitate. The presence of other intervening binary phases, 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 $\Delta H_f(Cd_3P_2)$ and $\Delta H_f(GeP)$ of Cd_3P_2 and GeP:

$$3\mu_{Cd} + 2\mu_P \leq \Delta H_f(Cd_3P_2), \qquad (3)$$

$$\mu_{Ge} + \mu_P \leq \Delta H_f(GeP), \qquad (4)$$

to find the allowed range for μ_{Cd} and μ_{Ge} in $CdGeP_2$. The electrons ionized upon forming a positively charged defect join the Fermi sea so the formation energy increases 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. Equations (2)–(4) were solved using the experimental values [15,16] of the formation energies for the binary phases Cd_3P_2 (-1.2 eV) and GeP (-0.3 eV), while a value of -1.5 eV, in the same range as other chalcopyrites [17], was used for $CdGeP_2$.

The allowed range of chemical potentials 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 : Cd rich, Ge poor;

point : Cd rich, Ge-rich; and point : 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 substitutional defects Mn_{Ge} and Mn_{Cd} at the chemical potentials , , and of Fig. 1 as a function of the Fermi energy. The vertical dashed line denotes the generalized gradient approximation (GGA) gap which is underestimated with respect to the experimental 1.72 eV gap. Transition points between charge states are indicated by solid circles. The defects can
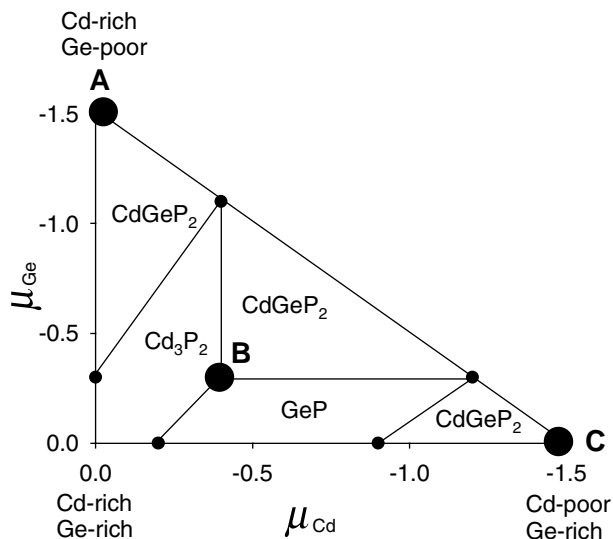

FIG. 1.   The range of Cd and Ge chemical potentials where $CdGeP_2$, GeP, and Cd_3P_2 are stable.

in these conditions has no holes and so cannot promote antiferromagnetism. (v)Ge-on-Cd antisite has high formation energy, and would therefore not have appreciable concentration.

Having identified the hole-producing centers that can yield FM, we next examine the predicted solubilities of isolated Mn. Our calculated formation energies for $CdGeP_2$:Mn and similar calculations for GaAs:Mn show consistently lower values (for the appropriate chemical potentials) in the former case, predicting higher Mn solubility: The lowest formation energy of substituting a Ga atom with Mn in GaAs is 1.0 eV (under Mn-rich, Ga-poor conditions). In contrast, even in the worst-case scenarios, we find a

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