

FIG. 1. (Color online). The density functional calculated allowed chemical potential ranges (sum of all the colored parts

$$2\Delta\mu_{\text{Al}} + \Delta\mu_{\text{Cu}} \leq \Delta H_f(\text{Al}_2\text{Cu}). \quad (8)$$

As shown in Fig. 1, CuAlS_2 is unstable with respect to formation of Al_2S_3 in the upper white area of Fig. 1, i.e., under Al-rich condition, (AlS, AlCu, and Al_2Cu pose weaker constraints, and are included in the Al_2S_3 ranges in Fig. 1). CuAlS_2 is also unstable with respect to CuS or Cu_2S precipi-

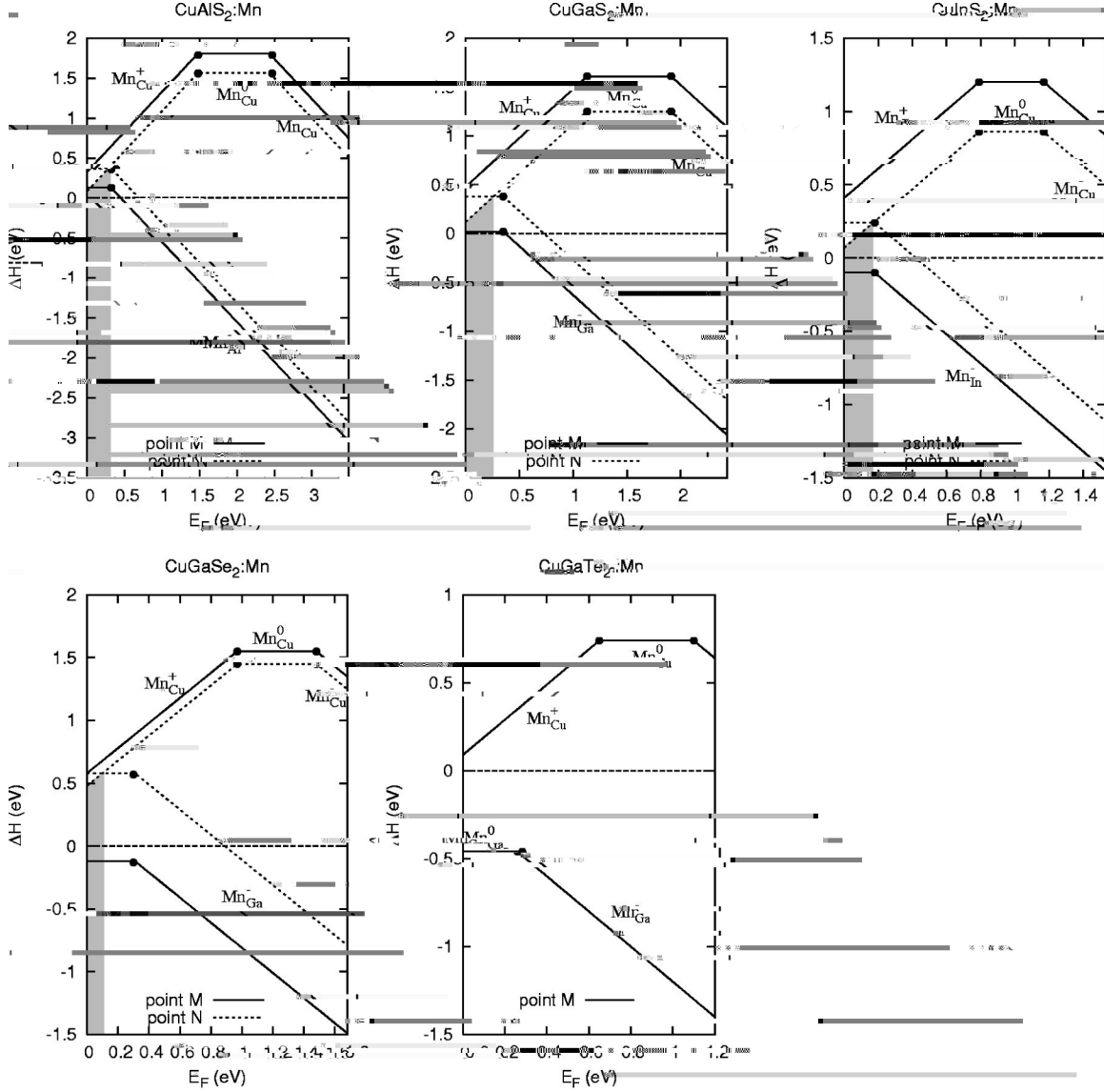


FIG. 2. The formation energy ΔH vs Fermi level for $\text{CuAlS}_2\text{:Mn}$, $\text{CuGaS}_2\text{:Mn}$, $\text{CuInS}_2\text{:Mn}$, $\text{CuGaSe}_2\text{:Mn}$, and $\text{CuGaTe}_2\text{:Mn}$ with the chemical potentials at point *M* and *N* in Fig. 1. Mn prefers to III sites at point *M*, independent of E_F , while it prefers the Cu site at point *N* only in the shaded E_F ranges. For $\text{CuGaTe}_2\text{:Mn}$, Mn on Cu is unstable for all E_F

IV. SITE PREFERENCE OF Mn IN CHALCOPYRITES

Having calculated the chemical potential domains for CuAlS_2 , CuGaS_2 , CuInS_2 , and CuGaSe_2 (Fig. 1), we next discuss the site preference of Mn in these chalcopyrites. The formation enthalpy for Mn substituting either the Cu or the III sites at different charge state are calculated using a single Mn atom in a 64 atom supercell according to^{16,17}

$$\Delta H_f^{(\alpha,q)} = E(\alpha,q) - E(0) + \sum_{\alpha} n_{\alpha} (\Delta\mu_{\alpha} + \mu_{\alpha}^{\text{Solid}}) + q(E_{VBM} + E_F), \quad (12)$$

where $E(\alpha,q)$ and $E(0)$ are the total energy of the supercell with and without defect α . Here $(\Delta\mu_{\alpha} + \mu_{\alpha}^{\text{Solid}})$ is the absolute value of the chemical potential of atom α . Also n_{α} is the

number of atoms for each defect; $n_{\alpha} = -1$ if an atom is added, while $n_{\alpha} = 1$ if an atom is removed. E_{VBM} represents the energy of the VBM of the defect-free system (which we take from the averaged eigenvalue of special k points) and E_F is the Fermi energy relative to the E_{VBM} . The atomic structure was fully relaxed in our calculation. The relaxation energy due to Mn substitution was 20–100 meV. The total energy of charged defects in a supercell calculation includes an error due to image charge interaction from periodic boundary condition. We therefore correct $E(\alpha,q)$ up to quadrupole term according to the Makov-Payne scheme.¹⁸ The correction raised $E(\alpha,q)$ by 120 to 300 meV for both $q=1$ and $q=-1$ charge states.

The functional relations between the formation energy and chemical potentials and E_F at different charge states are listed in Table II. The site preference of Mn is determined by

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