

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,  $\text{CuAlS}_2$  is unstable with respect to formation of  $\text{Al}_2\text{S}_3$  in the upper white area of Fig. 1, i.e., under Al-rich condition, (AlS, AlCu, and  $\text{Al}_2\text{Cu}$  pose weaker constraints, and are included in the  $\text{Al}_2\text{S}_3$  ranges in Fig. 1).  $\text{CuAlS}_2$  is also unstable with respect to CuS or  $\text{Cu}_2\text{S}$  precipi-



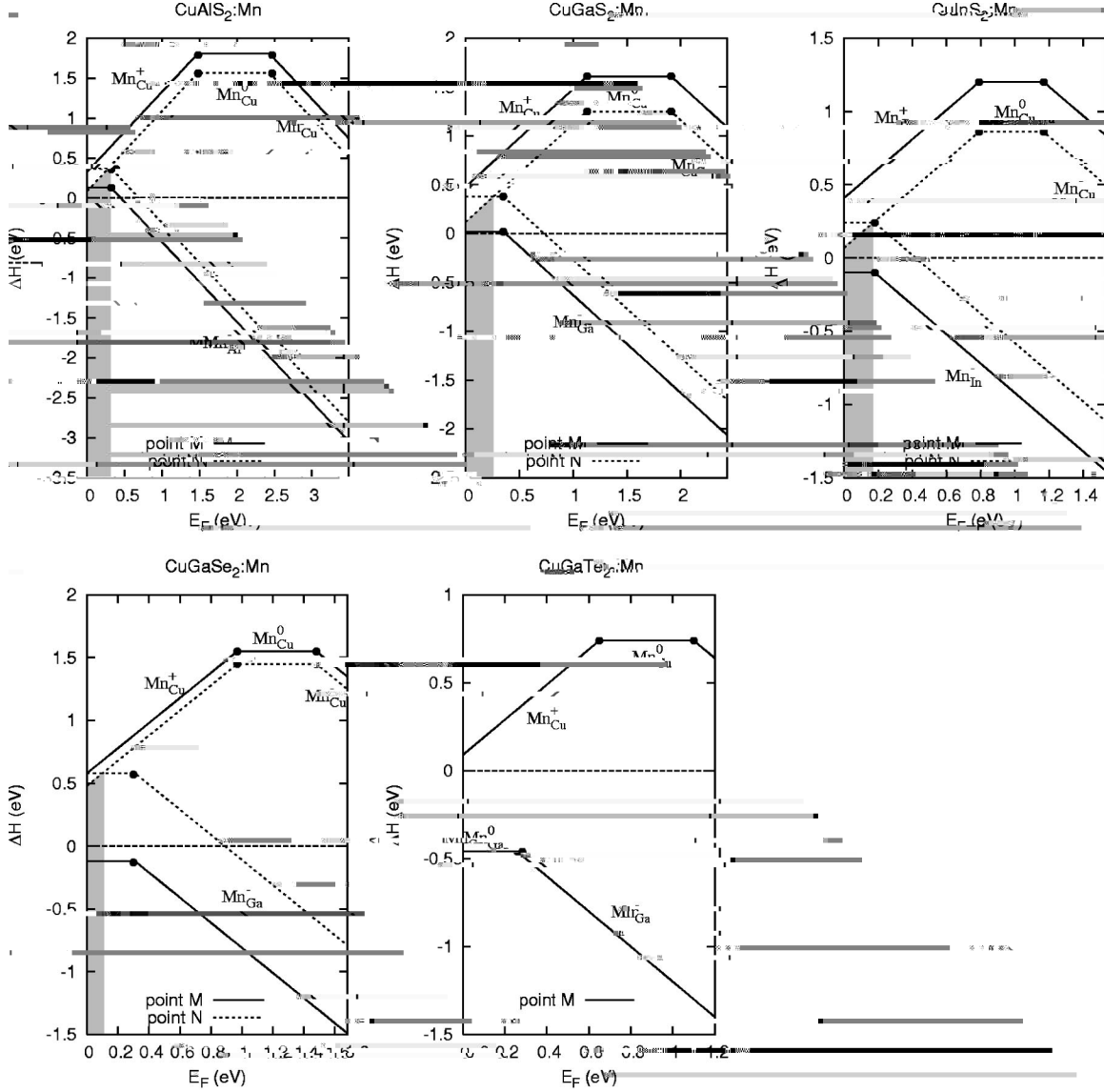


FIG. 2. The formation energy  $\Delta H$  vs Fermi level for  $\text{CuAlS}_2\text{:Mn}$ ,  $\text{CuGaS}_2\text{:Mn}$ ,  $\text{CuInS}_2\text{:Mn}$ ,  $\text{CuGaSe}_2\text{:Mn}$ , and  $\text{CuGaTe}_2\text{:Mn}$  with the chemical potentials at point *M* and *N* in Fig. 1. Mn prefers to III sites 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  $\text{CuAlS}_2$ ,  $\text{CuGaS}_2$ ,  $\text{CuInS}_2$ , and  $\text{CuGaSe}_2$  (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<sup>16,17</sup>

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

where  $E(\alpha,q)$  and  $E(0)$  are the total energy of the supercell with and without defect  $\alpha$ . Here  $(\Delta\mu_{\alpha} + \mu_{\alpha}^{\text{Solid}})$  is the absolute value of the chemical potential of atom  $\alpha$ . Also  $n_{\alpha}$  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.<sup>18</sup> 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



- <sup>17</sup>S.B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **78**, 4059 (1997).
- <sup>18</sup>G. Makov and M.C. Payne, Phys. Rev. B **51**, 4014 (1995).
- <sup>19</sup> $Mn_{III}(0/-)$  means the Fermi energy at which  $\Delta H(Mn_{III}, q=0) = \Delta H(Mn_{III}, q=-)$ , see Fig. 2. When  $E_F$  is below  $Mn_{III}(0/-)$ , charges at  $Mn_{Cu}^+$  can not be balanced since  $Mn_{III}$  is at neutral state; when  $E_F$  is beyond  $Mn_{III}(0/-)$  charges at  $Mn_{III}^-$  can not be neutralized since  $Mn_{III}^-$  has more population than  $Mn_{Cu}$ .
- <sup>20</sup>M. Sugiyama, R. Nakai, and H.N.S.F. Chichibu, J. Appl. Phys. **92**, 7317 (2002).
- <sup>21</sup>I. Aksenov and K. Sato, Jpn. J. Appl. Phys., Part 1 **31**, 2352 (1992).
- <sup>22</sup>K.G. Lisunov, E. Arushanov, G.A. Thomas, E. Bucher, and J.H. Schön, Phys. Rev. Lett. **88**, 047205 (2002).
- <sup>23</sup>B. Koscielniak-Mucha and A. Opanowicz, Phys. Status Solidi A **130**, K55 (1992).
- <sup>24</sup>C. Kittel, *Introduction to Solid State Physics* 4th ed. (Wiley, New York 1971).
- <sup>25</sup>P. Villars and L. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (American Society for Metals, Metals Park, OH, 1985), Vol. I.
- <sup>26</sup>T. Asada and K. Terakura, Phys. Rev. B **47**, 15 992 (1993).
- <sup>27</sup>Using the same structure of  $Ga_2Se_3$ , see Ref. 28.
- <sup>28</sup>K. U5236 450.246 656.535 g1(iley)64.7(,)-292.6(N)0.1(ew)]5NymyA.98 0W73