Electronic Supplementary Information (ESI) for

# Influence of Ge distribution on the first order magnetic transition of MnFe(P,Ge) magnetocaloric material

Zhenlu Zhang,[a] Danmin Liu,*[a] Weiqiang Xiao,[a] Hui Li,[a] Shaobo Wang,[a] Yuntian Liang,[a] Hongguo Zhang,[b] Shanlin Li,[a] Junjie Fu,[a] and Ming Yue[b]

[a] *Key Lab of Microstructure and Property of Advanced Material, Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100124, PRC*

[b] *Key Lab of Advanced Functional Materials, Ministry of Education, College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, PRC*

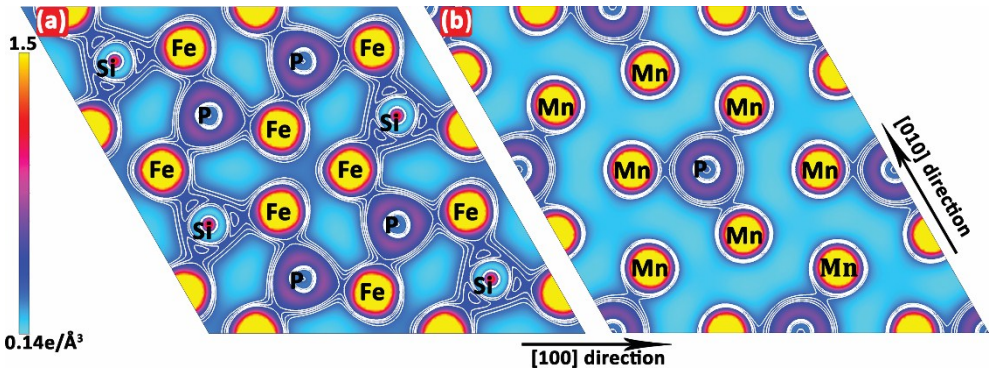


Fig. S1 Electron-density comparison for the FM phase of $MnFeP_{0.67}Si_{0.33}$ supercell with Si only filling the 2c site; (a) the (001) plane, (b) the (002) plane. The contour lines are drawn from 0.34 to 0.50 *e*/Å$^3$ with 0.04 *e*/Å$^3$ intervals.

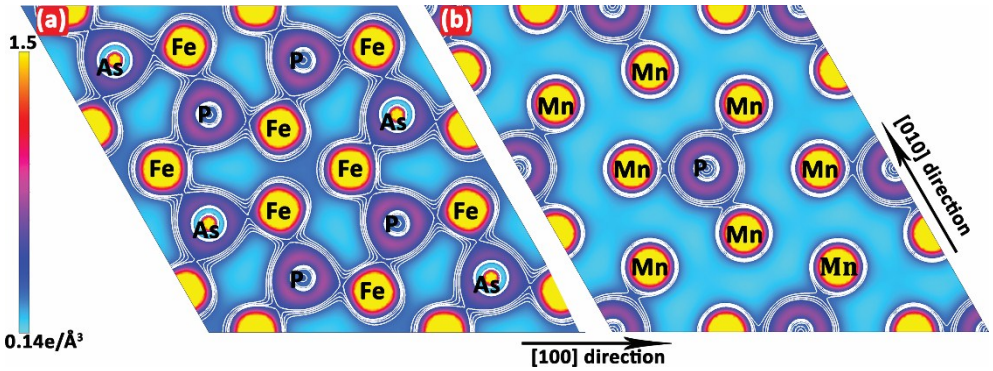


Fig. S2 Electron-density comparison for the FM phase of $MnFeP_{0.67}As_{0.33}$ supercell with As only filling the 2c site; (a) the (001) plane, (b) the (002) plane. The contour lines are drawn from 0.34 to 0.50 *e*/Å$^3$ with 0.04 *e*/Å$^3$ intervals.

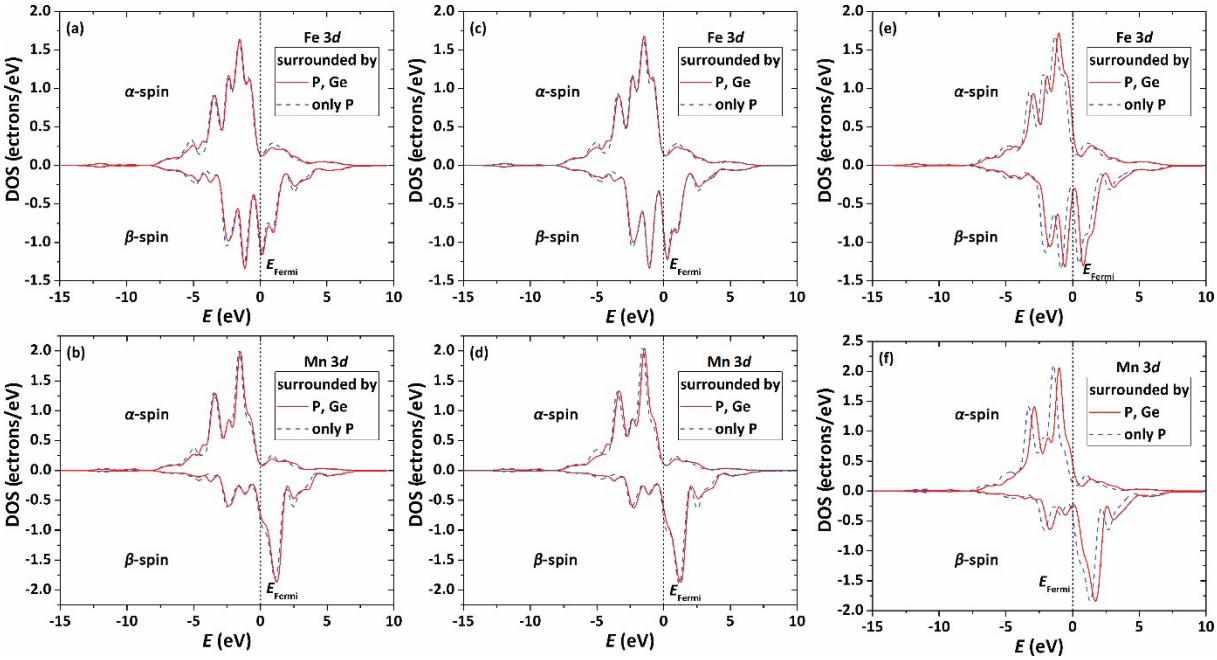


Fig. S3 Fe 3*d* and Mn 3*d* density of states for the supercell of $MnFeP_{1-x}Ge_x$ ($x$ = 1/6, 1/4, and 5/12) with Ge occupying the 2c site; (a) and (b) $x$ = 1/6, (c) and (d) $x$ = 1/4, (e) and (f) $x$ = 5/12. The exchange splits of Fe and Mn 3*d* across the Fermi level are enhanced with increasing Ge content.

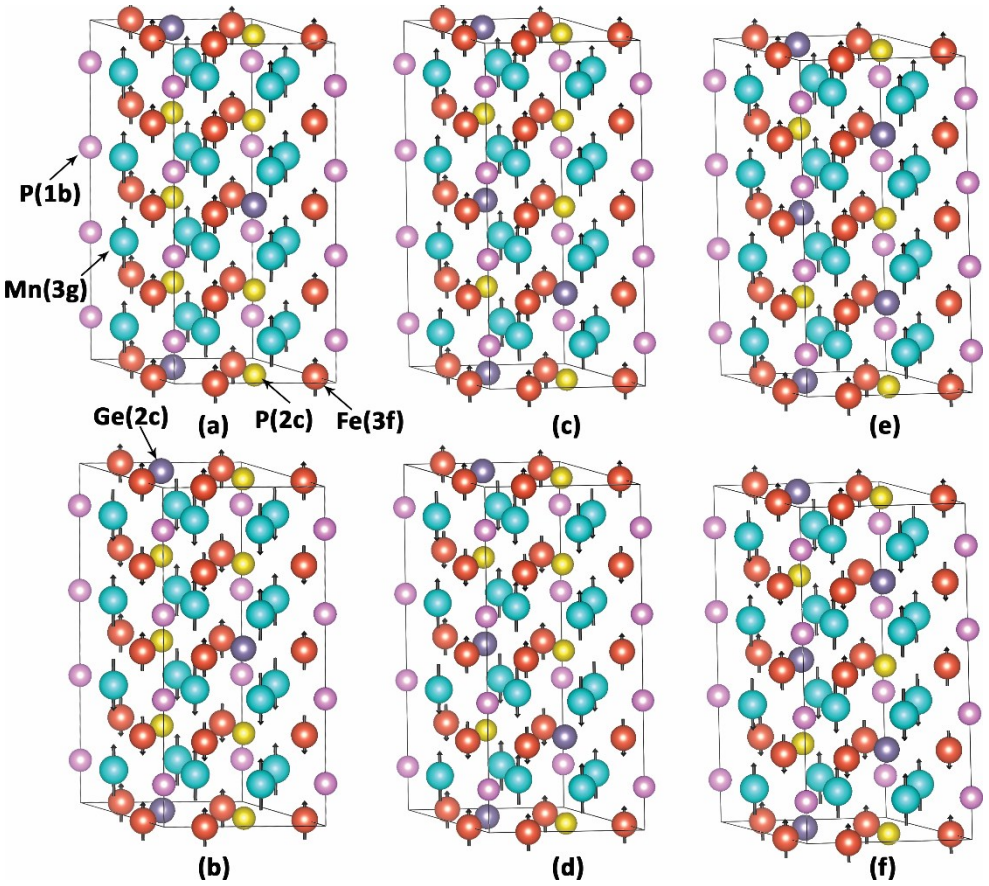


Fig. S4 Virtual FM and AFM structures for $MnFeP_{1-x}Ge_x$ ($x$ = 1/6, 1/4, and 1/3); (a) and (b) $x$ = 1/6, (c) and (d) $x$ = 1/4, (e) and (f) $x$ = 1/6. The top and bottom rows are for the FM and AFM structures.

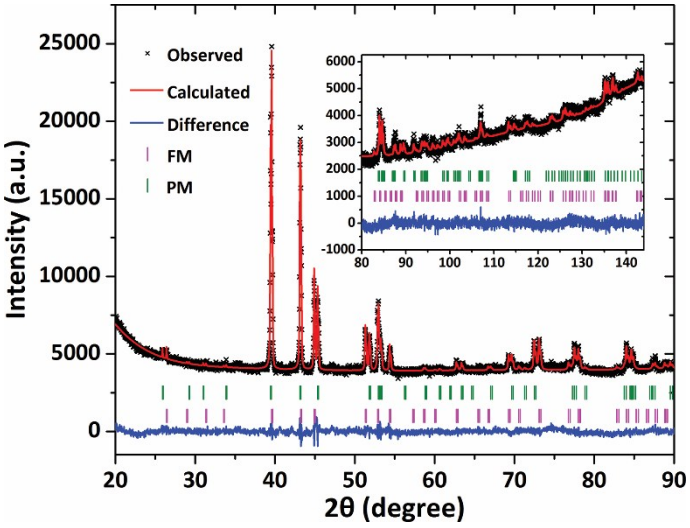


Fig. S5 Observed and calculated powder X-ray patterns for a coexistence state of $MnFeP_{0.74}Ge_{0.26}$ at 355 K. The high angle region is enlarged in the inset.

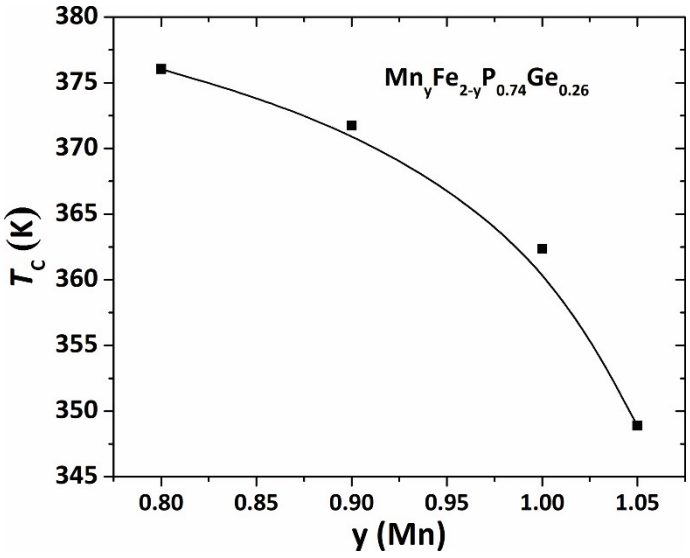


Fig. S6 Mn content dependence of the transition temperature determined upon heating of DSC for $Mn_yFe_{2-y}P_{0.74}Ge_{0.26}$ ($y$ = 0.80, 0.90, 1.00, and 1.05) compounds.

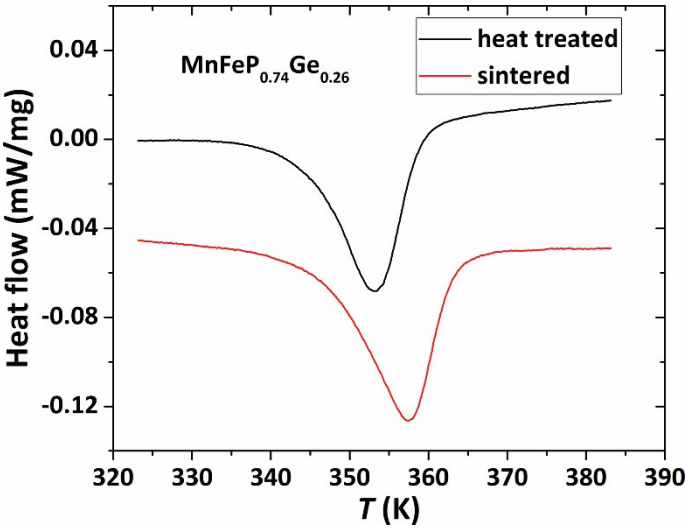


Fig. S7 The heat flow upon cooling for the heat-treated and sintered samples of $MnFeP_{0.74}Ge_{0.26}$ compound.