Magnetic Behavior of Bimetallic Layered Phases

$M'_{0.2}Mn_{0.8}PS_3$ ($M' = Zn^{II}$, Cu^{II}, Ni^{II}, Co^{II})

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Fig. S1. Arrangement of Mn(II) ions and vacancies in the potassium precursor $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$, as determined by neutron diffraction (left) [1,2]; and proposed arrangement for Mn(II) and secondary transition metal ions in the studied bimetallic phases (right)

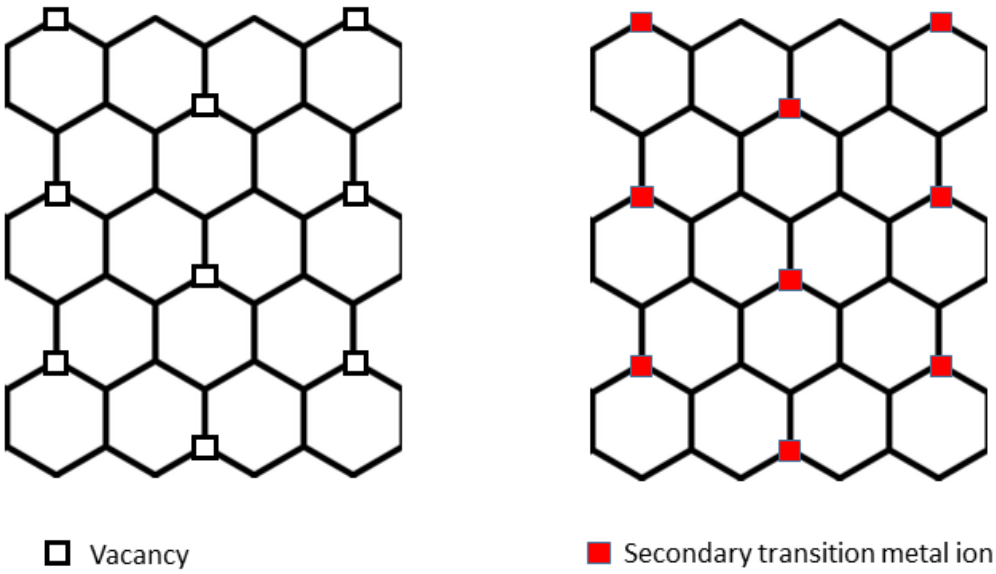


Fig. S2: Magnetic susceptibility plots $\chi_M(T)$ and $\chi_M^{-1}(T)$ of (a) $Zn_{0.2}Mn_{0.8}PS_3{\cdot}0.25H_2O$, (b) $Ni_{0.2}Mn_{0.8}PS_3{\cdot}0.25H_2O$ and (c) $Co_{0.2}Mn_{0.8}PS_3{\cdot}0.25H_2O$. The red lines are the least−square fit with Eq (2) as described in text. The blue line is the least square fit with Eq (4) as described in the text.

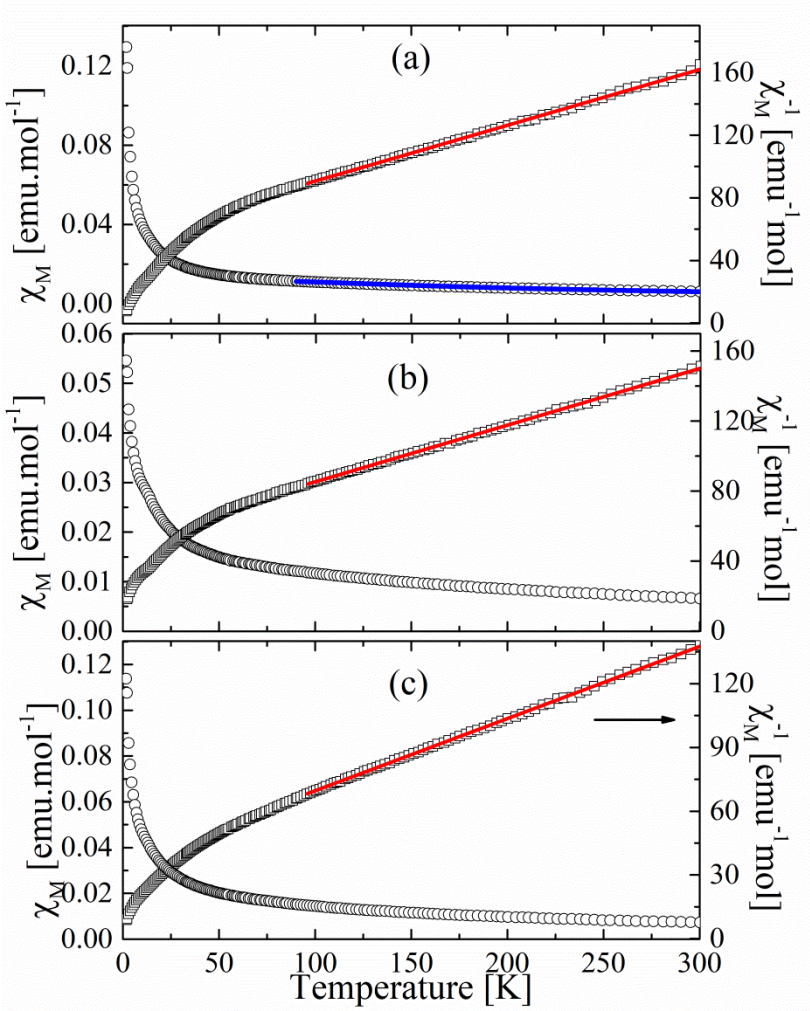


Fig. S3: FC and ZFC susceptibility curves of (a) $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, (b) $Cu_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, (c) $Ni_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ and (d) $Co_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$.

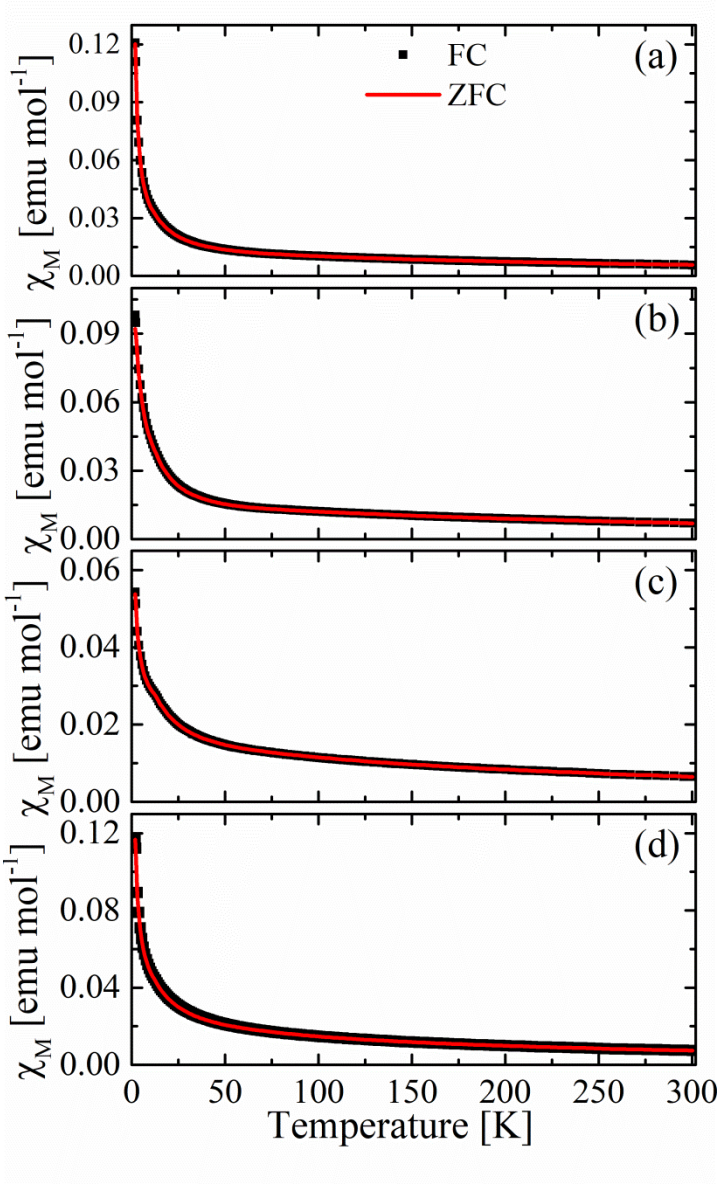


Fig. S4: (a) to (c) Field dependence of magnetization; and (d) to (f) first derivative curves. Measurements made for $Zn_{0.2}Mn_{0.8}PS_3$, $Ni_{0.2}Mn_{0.8}PS_3$ and $Co_{0.2}Mn_{0.8}PS_3$ at different temperatures.

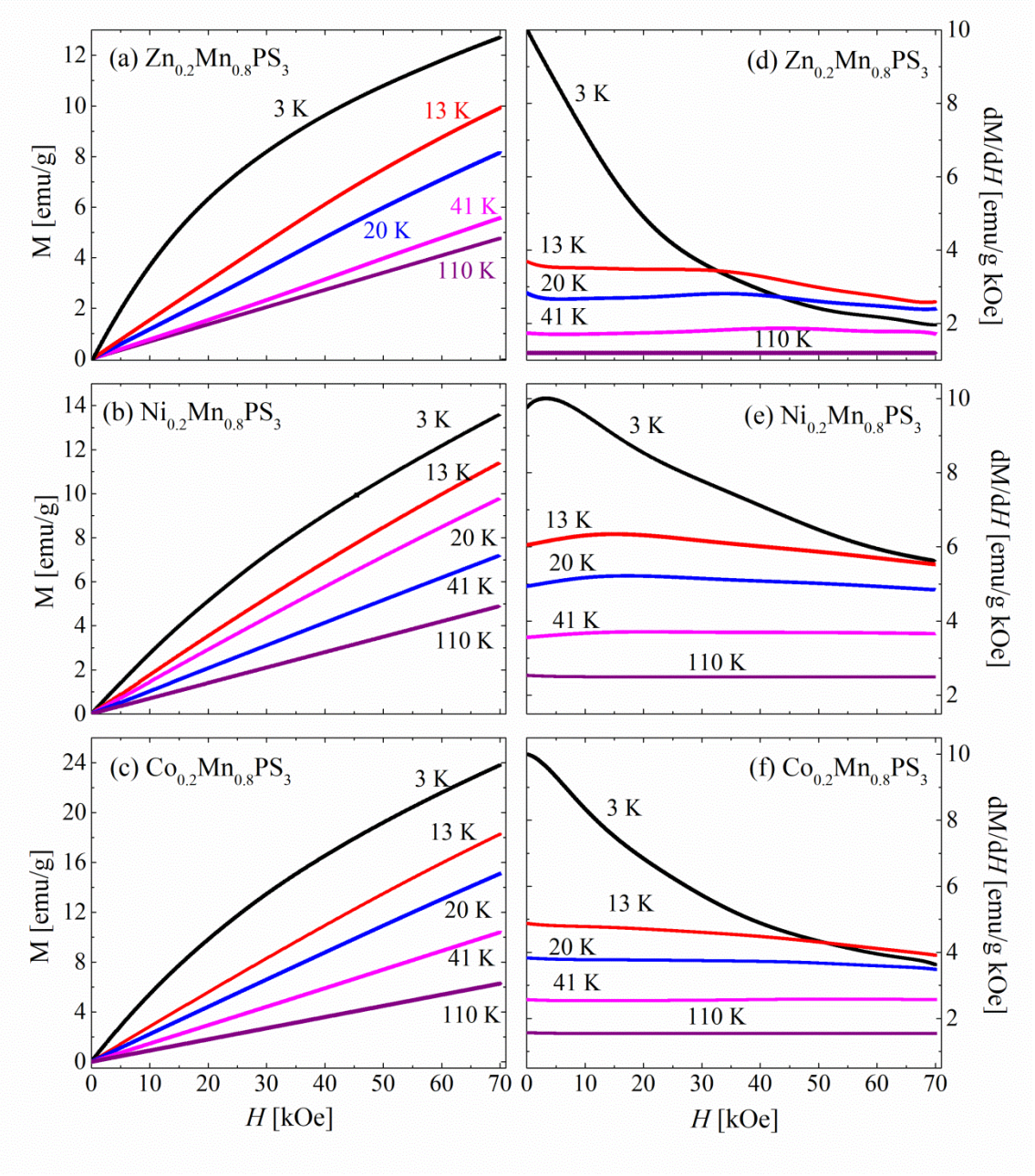


Fig. S5: EPR spectra of (a) $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ and (b) $Ni_{0.2}Mn_{0.8}PS3 \cdot 0.25H_2O$.

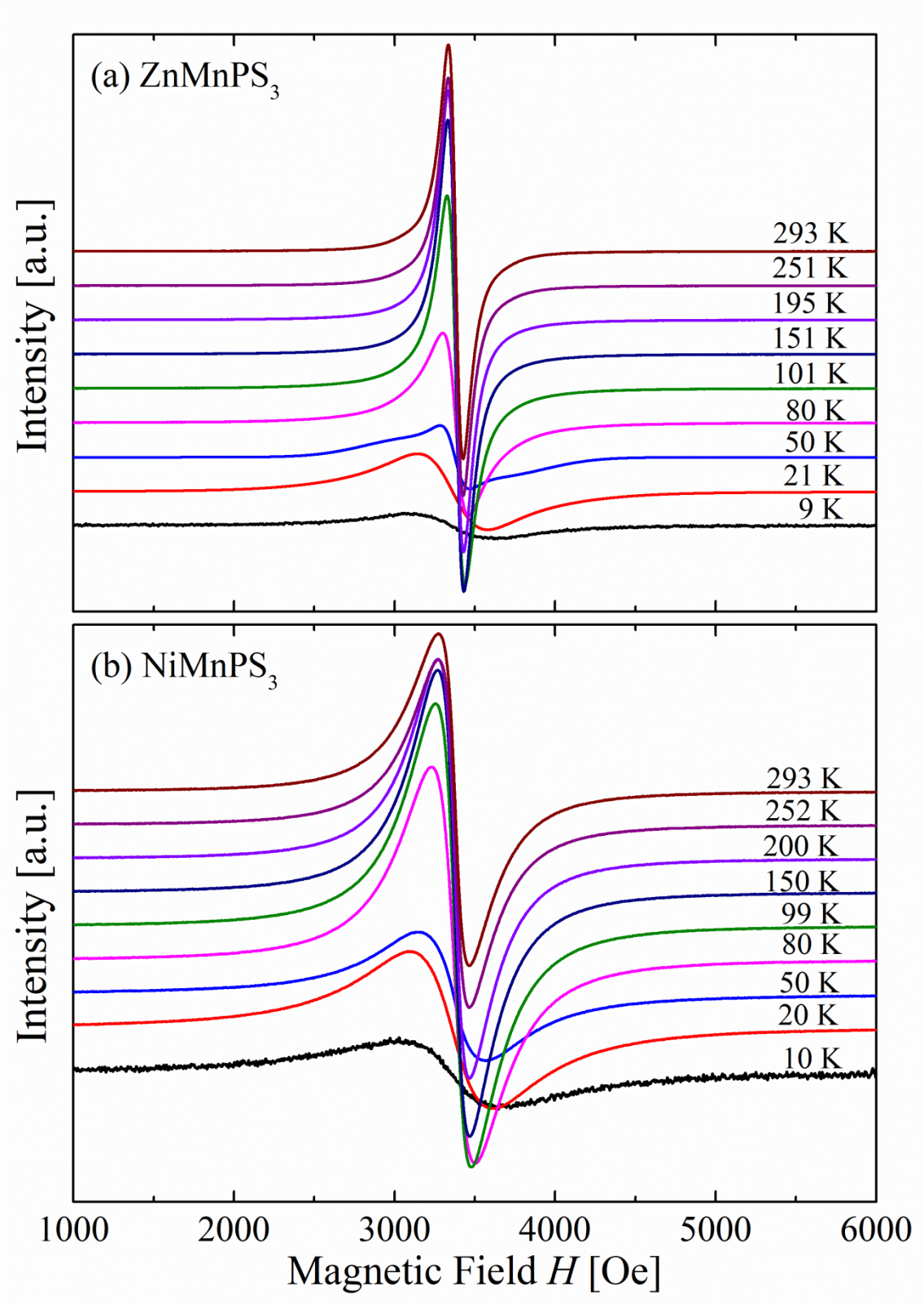


Fig. S6. $I_{DIN}(T)$ of the studied phases.

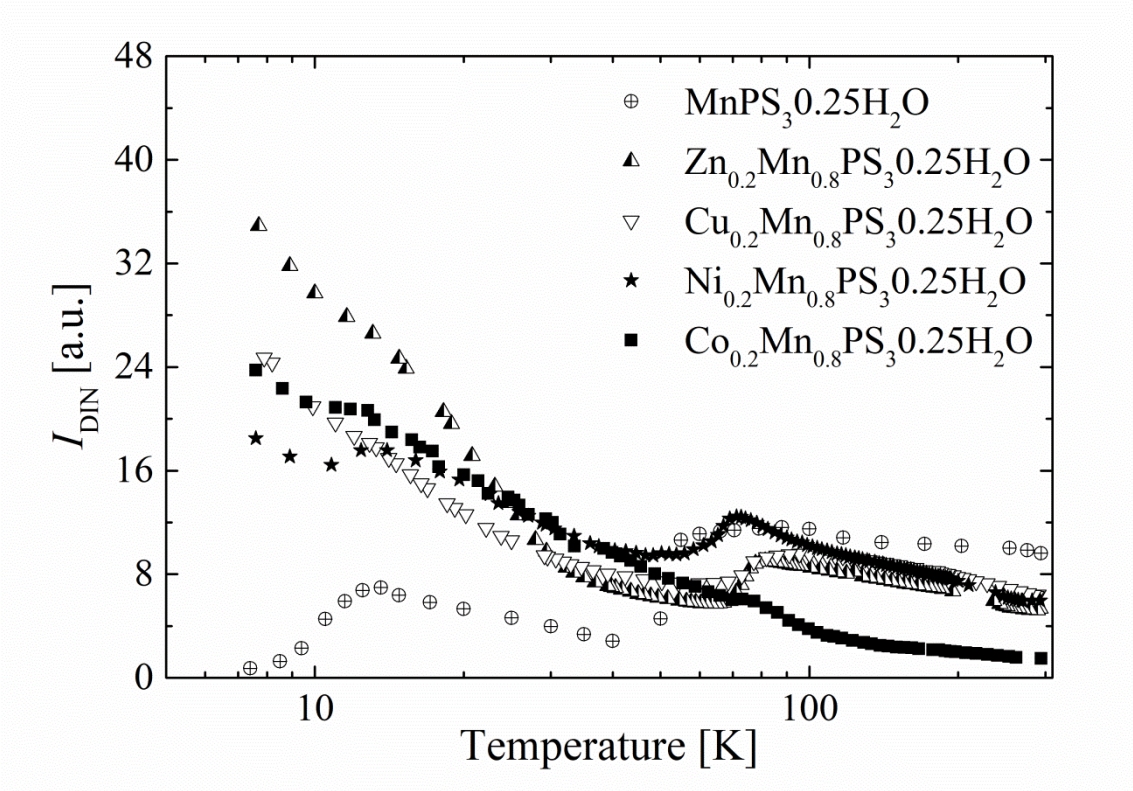
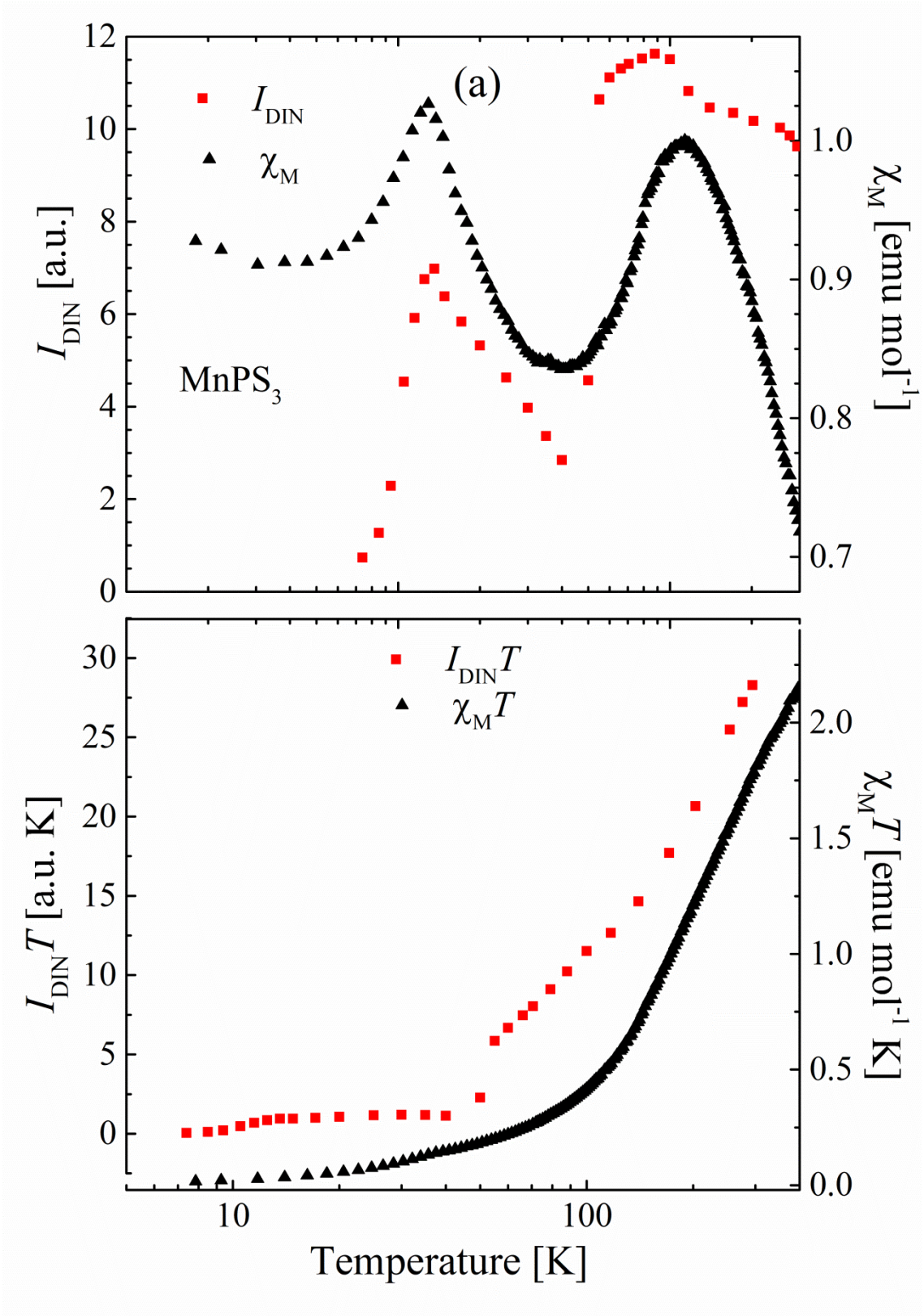
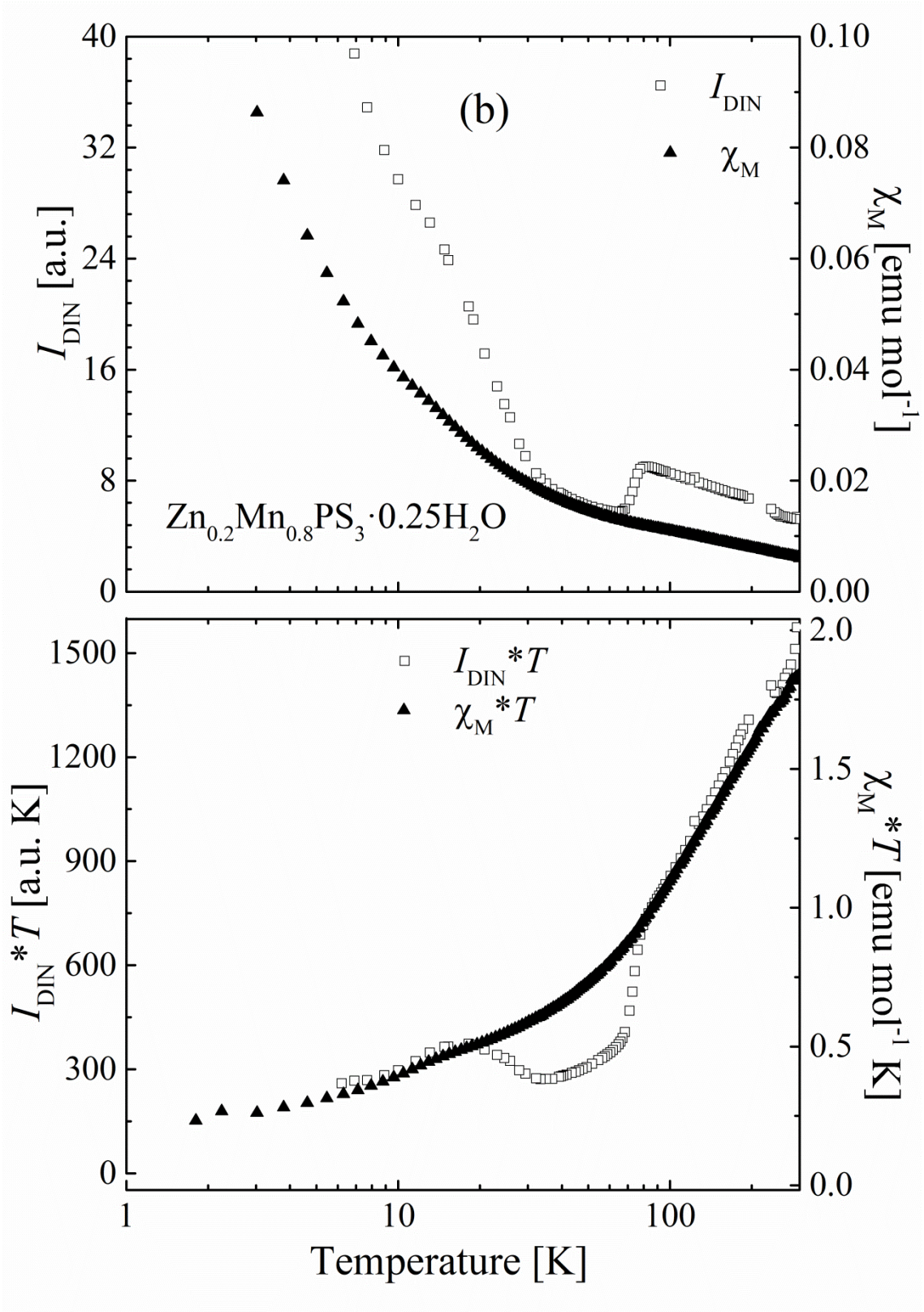
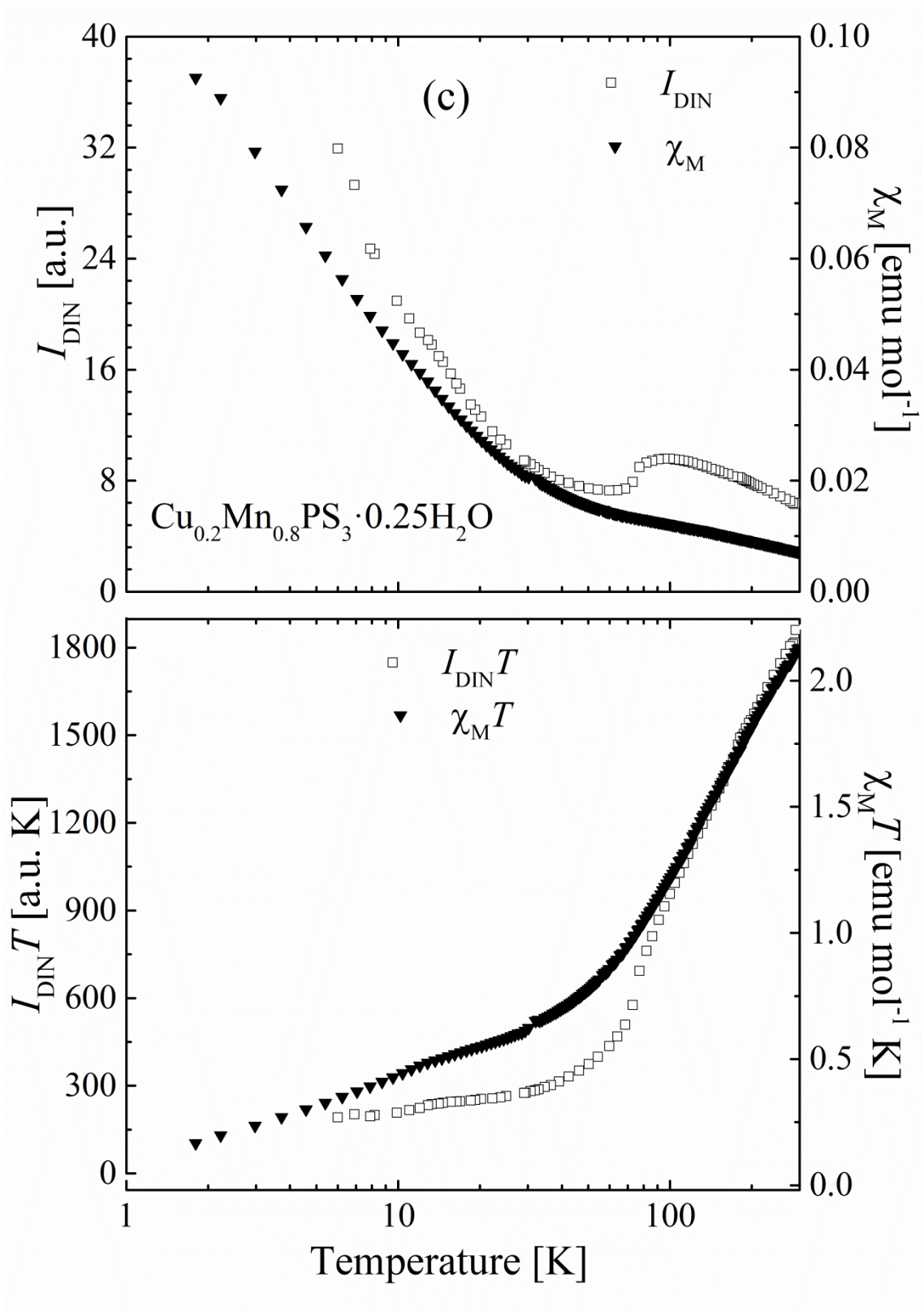
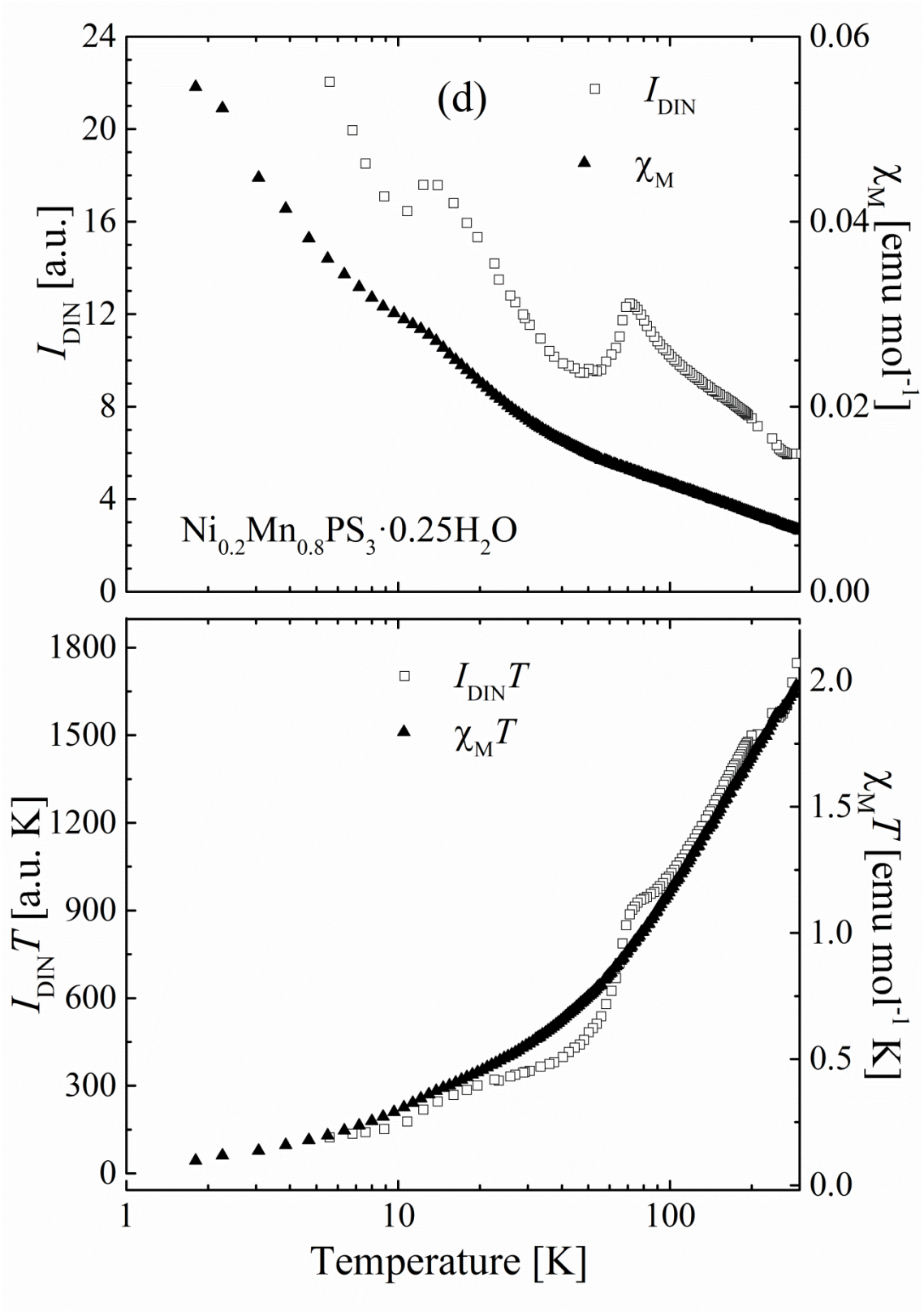


Fig. S7: Comparisons between EPR intensities after double integration (I_{DIN}) with magnetic susceptibility data (χ_M), and EPR intensities ($I_{DIN}T$) with magnetic susceptibility ($\chi_M T$) temperature product data of pristine and bimetallic phases: (a) $MnPS_3$, (b) $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, (c) $Cu_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, (d) $Ni_{0.2}Mn_{0.8}PS3 \cdot 0.25H_2O$ and (e) $Co_{0.2}Mn_{0.8}PS3 \cdot 0.25H_2O$.




(b)
I_{DIN}
χ_M
$Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$
I_{DIN} [a.u.]
χ_M [emu mol^{-1}]
$I_{DIN}*T$
χ_M*T
$I_{DIN}*T$ [a.u. K]
χ_M*T [emu mol^{-1} K]
Temperature [K]


(c)
I_{DIN}
χ_M
$Cu_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$
I_{DIN} [a.u.]
χ_M [emu mol^{-1}]
$I_{DIN}T$
$\chi_M T$
$I_{DIN}T$ [a.u. K]
$\chi_M T$ [emu mol^{-1} K]
Temperature [K]


(d)
I_{DIN}
χ_M
$Ni_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$
I_{DIN} [a.u.]
χ_M [emu mol^{-1}]
$I_{DIN}T$
$\chi_M T$
$I_{DIN}T$ [a.u. K]
$\chi_M T$ [emu mol^{-1} K]
Temperature [K]

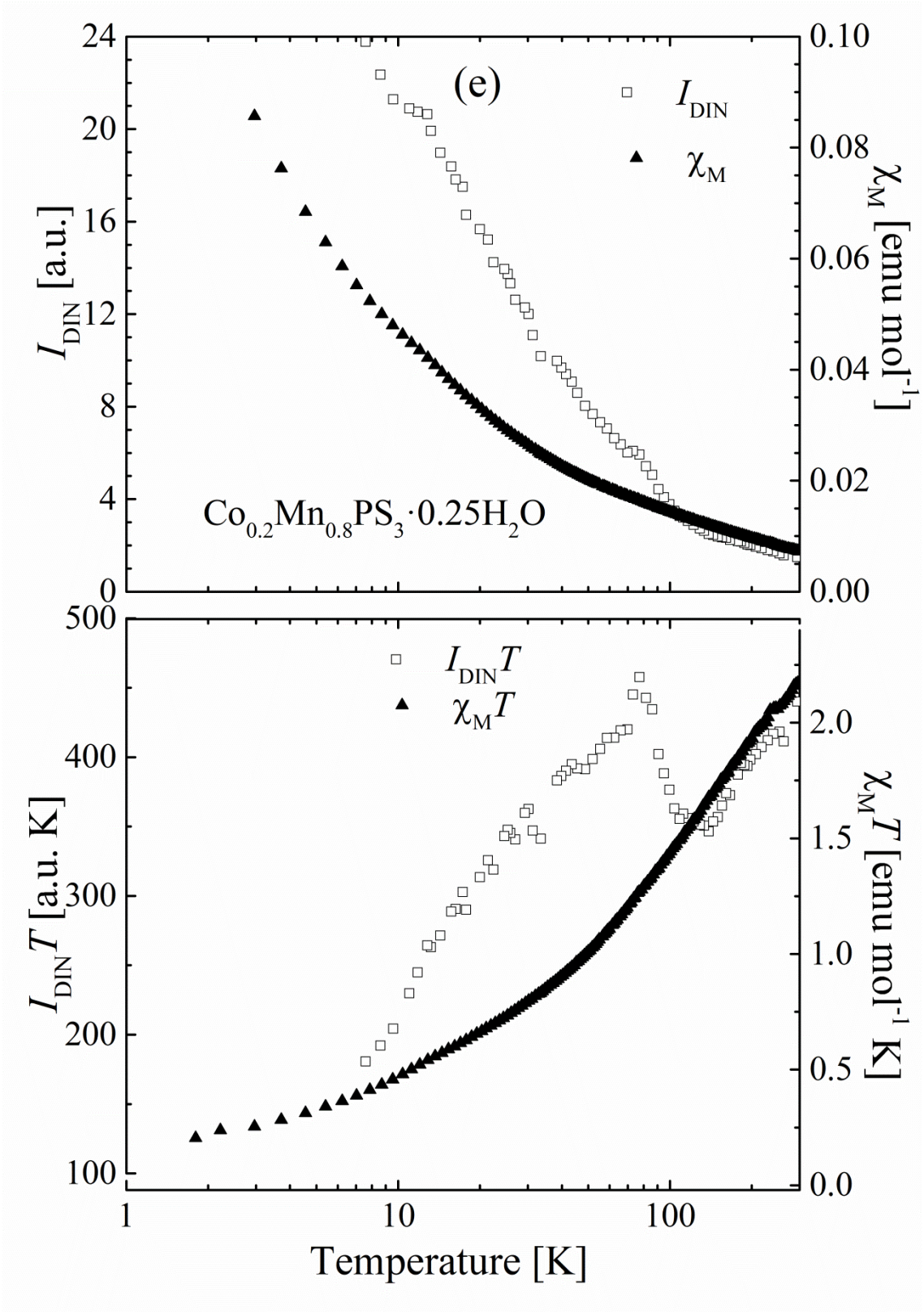
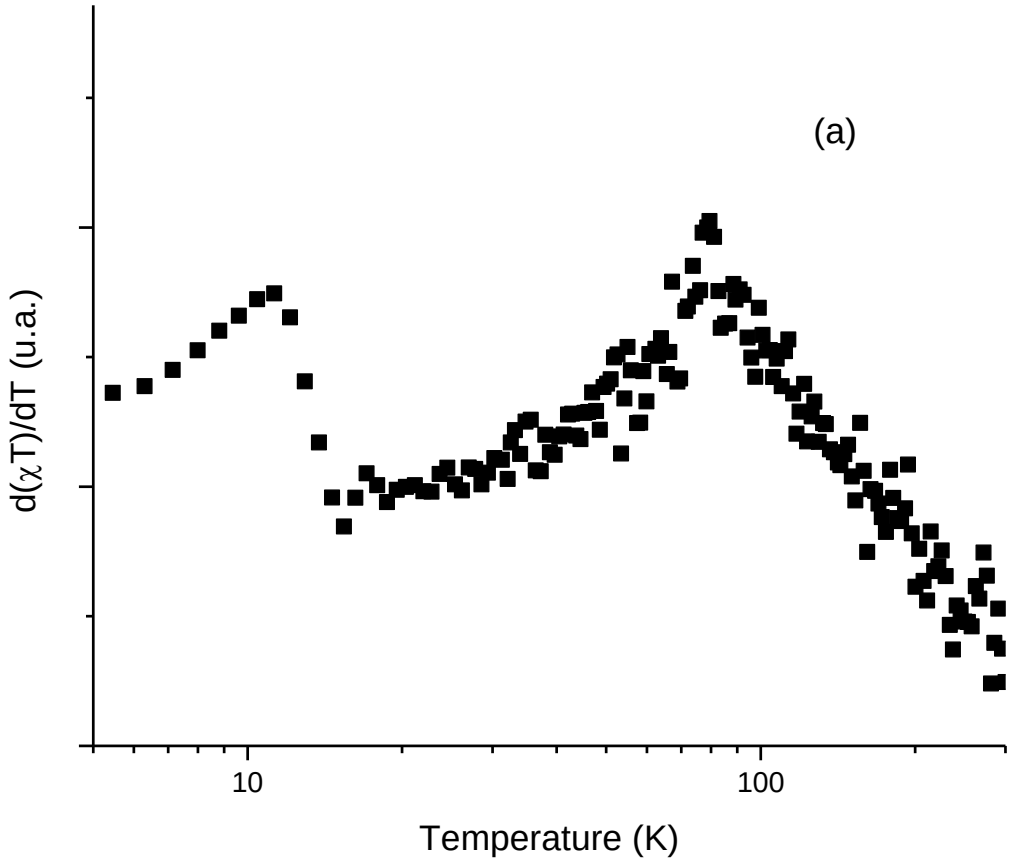
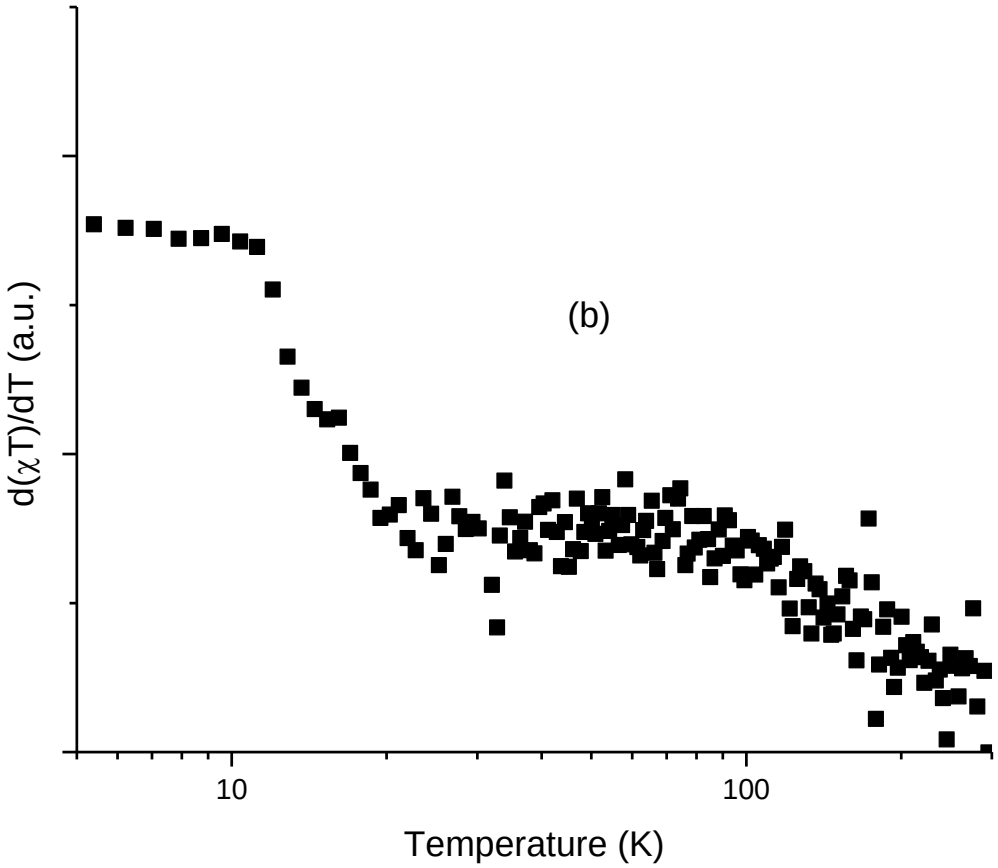
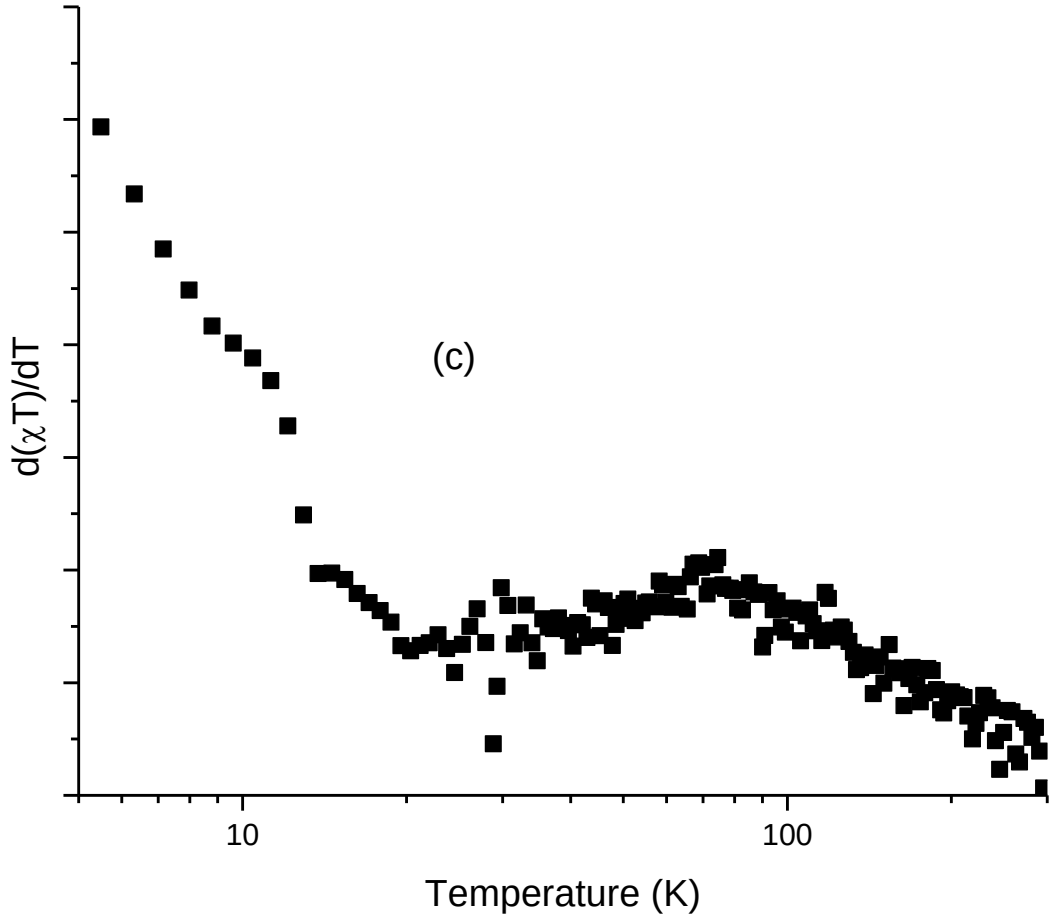
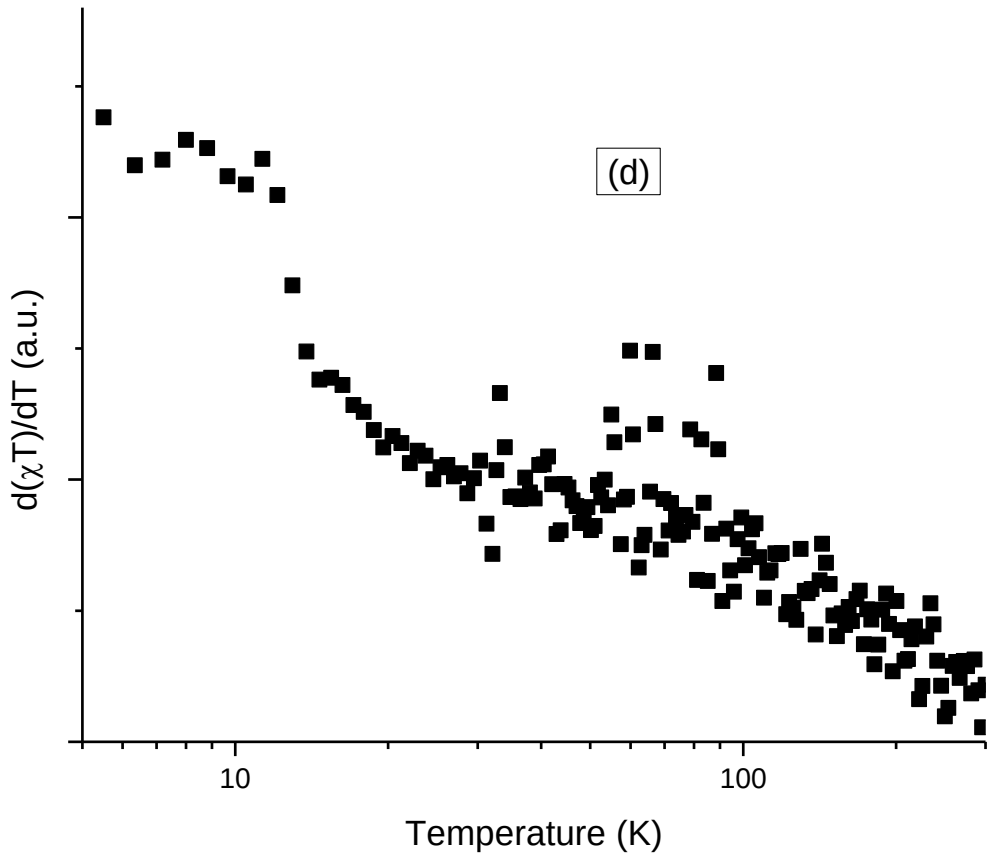

(e)
I_{DIN}
χ_M
$Co_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$
I_{DIN} [a.u.]
χ_M [emu mol^{-1}]
$I_{DIN}T$
$\chi_M T$
$I_{DIN}T$ [a.u. K]
$\chi_M T$ [emu mol^{-1} K]
Temperature [K]

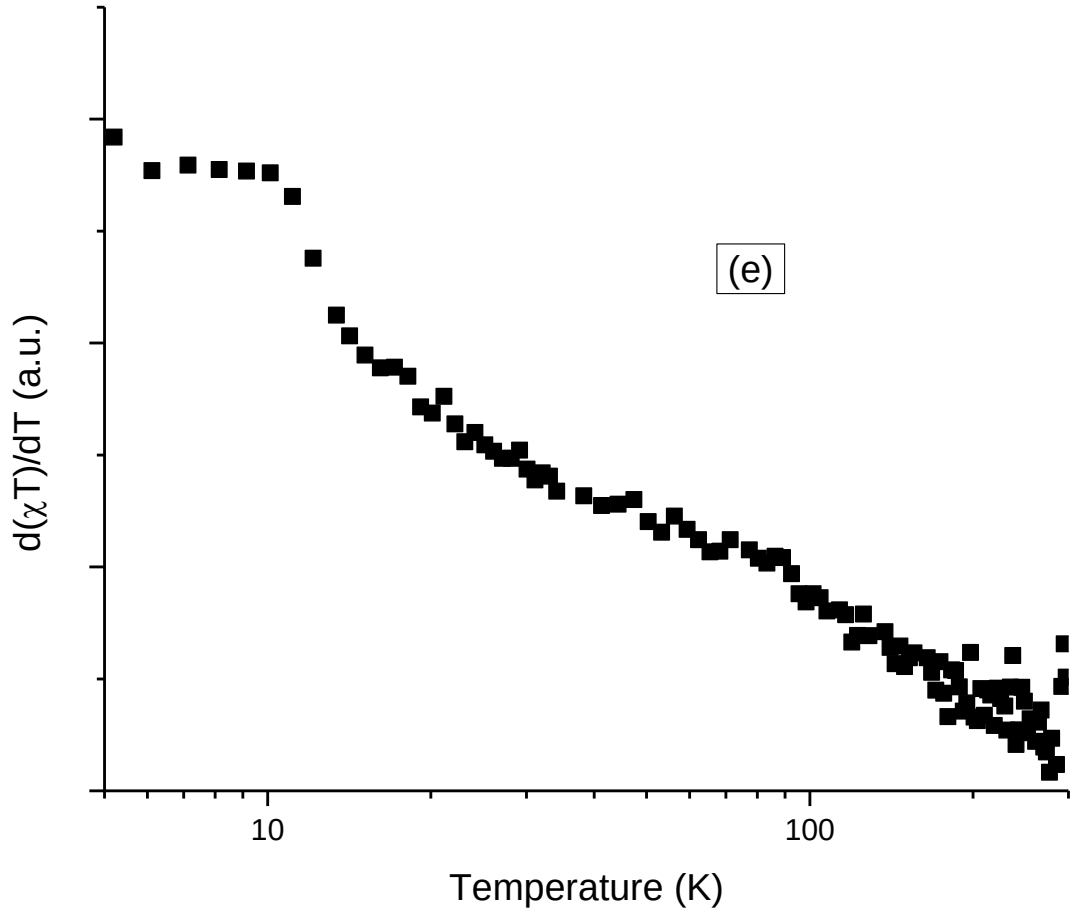
Fig S8. First derivative of the χT(T) plot for the pristine and bimetallic phases: (a) $MnPS_3$, (b) $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, (c) $Cu_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, (d) $Ni_{0.2}Mn_{0.8}PS3 \cdot 0.25H_2O$ and (e) $Co_{0.2}Mn_{0.8}PS3 \cdot 0.25H_2O$.




d(χT)/dT (a.u.)
(b)
10
100
Temperature (K)


d(χT)/dT
(c)
10
100
Temperature (K)


(d)
d(χT)/dT (a.u.)
10
100
Temperature (K)



(1) Evans, J. S. O.; O'Hare, D.; Clement, R. The Structure of Co(.eta.-C5H5)2+ and NMe4+ Intercalates of MnPS3: An X-Ray, Neutron-Diffraction, and Solid-State NMR Study. *J. Am. Chem. Soc.* **1995**, *117* (16), 4595–4606 DOI: 10.1021/ja00121a017.

(2) Evans, J. S. O.; O'Hare, D.; Clement, R.; Leaustic, A.; Thuéry, P. Origins of the Spontaneous Magnetization in MnPS3 Intercalates: A Magnetic Susceptibility and Powder Neutron Diffraction Study. *Adv. Mater.* **1995**, *7* (8), 735–739 DOI: 10.1002/adma.19950070812.