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Charge-transfer phase transition and zero thermal expansion in cesium manganese hexacyanoferrates

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Phase transition temperatures of $Cs_xMn[Fe(CN)_6]_y \cdot zH_2O$:

Table S1. The phase transition temperatures of the $Cs_xMn[Fe(CN)_6]_y \cdot zH_2O$ at a cooling and warming rates of 0.5 $Kmin^{-1}$.

Sample		$T_{1/2\downarrow}$ / K	$T_{1/2\uparrow}$ / K
⇒ **1**.	$Cs^{I}_{1.78}Mn^{II}[Fe^{II}(CN)_6]_{0.78}[Fe^{III}(CN)_6]_{0.22}+0.35MnO_2$	207	225
	$Cs^{I}_{1.6}Mn^{II}[Fe^{II}(CN)_6]_{0.6}[Fe^{III}(CN)_6]_{0.4}+0.2MnO_2$	195	230
⇒ **2**.	$Cs^{I}_{1.57}Mn^{II}[Fe^{II}(CN)_6]_{0.57}[Fe^{III}(CN)_6]_{0.43}+0.24MnO_2$	190	231
	$Cs^{I}_{1.5}Mn^{II}[Fe^{II}(CN)_6]_{0.5}[Fe^{III}(CN)_6]_{0.5}+0.2MnO_2$	185	230
⇒ **3**.	$Cs^{I}_{1.51}Mn^{II}[Fe^{II}(CN)_6]_{0.51}[Fe^{III}(CN)_6]_{0.49}+0.19MnO_2$	175	233
	$Cs^{I}_{1.3}Mn^{II}[Fe^{II}(CN)_6]_{0.3}[Fe^{III}(CN)_6]_{0.7}+0.2MnO_2$	175	240
	$Cs^{I}_{1.1}Mn^{II}[Fe^{II}(CN)_6]_{0.25}[Fe^{III}(CN)_6]_{0.7} \cdot H_2O+0.1MnO_2$	–	–
⇒ **4**.	$Cs^{I}_{0.94}Mn^{II}[Fe^{II}(CN)_6]_{0.21}[Fe^{III}(CN)_6]_{0.70} \cdot 0.8H_2O$	– (140)*	– (230)*

* The phase transition temperatures at a cooling rate of –0.01 $Kmin^{-1}$.

O 1s XPS spectra:

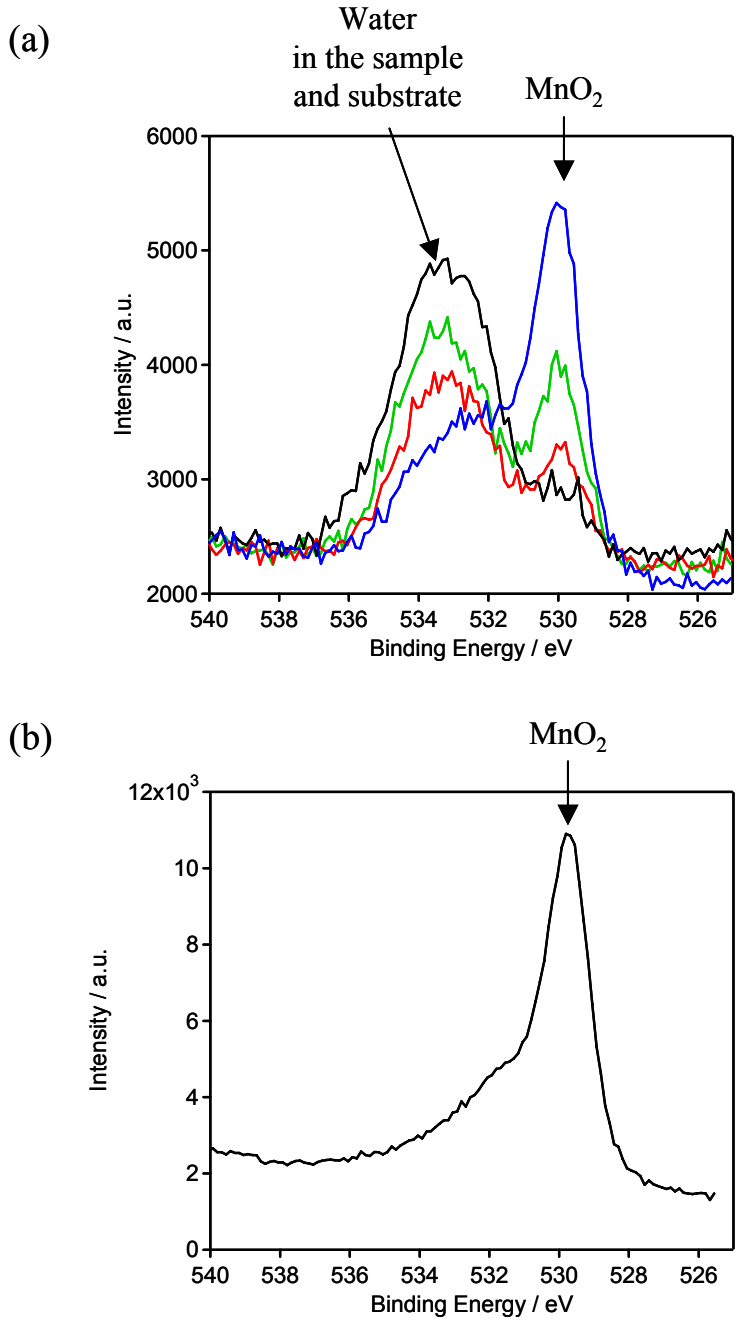

Fig. S1 (a) O1s XPS spectra for **1** (blue), **2** (green), **3** (red), and **4** (black); (b) O 1s spectra for MnO_2. The peak at 533.3 eV results from water contained in $Cs_xMn[Fe(CN)_6]_y{\cdot}zH_2O$ compounds and the substrate.

IR spectra, magnetic susceptibility, and XRD patterns for $Cs^{I}_{2}Mn^{II}[Fe^{II}(CN)_6]\cdot 3.5H_2O$:

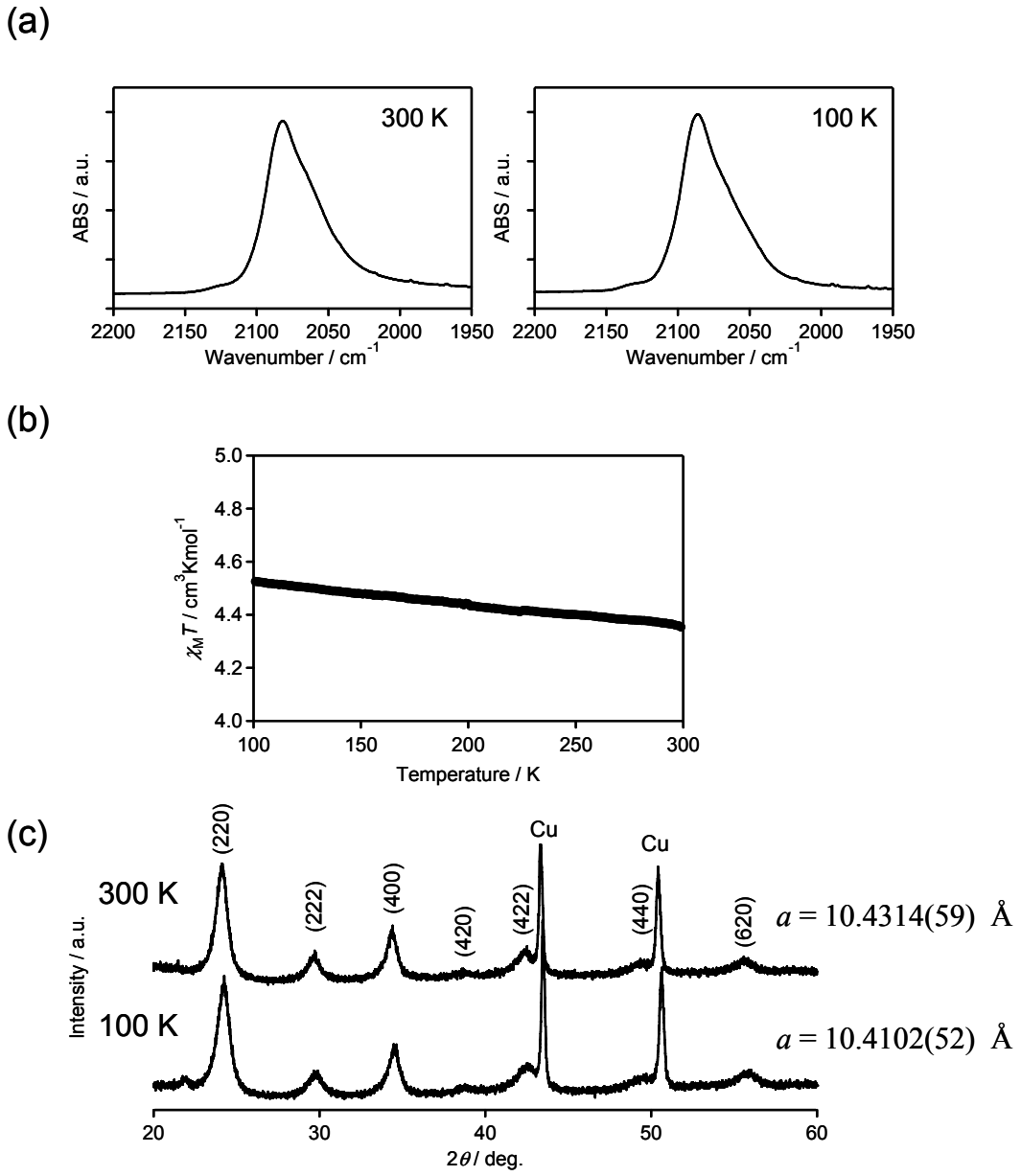

Fig. S2 (a) IR spectra at 300 K (right) and 100 K (left), (b) $\chi_M T$-T plots, and (c) XRD patterns at 300 K (upper) and 100 K (lower) of $Cs^{I}Mn^{II}[Fe^{II}(CN)_6]\cdot 3.5H_2O$.

Weiss temperature:

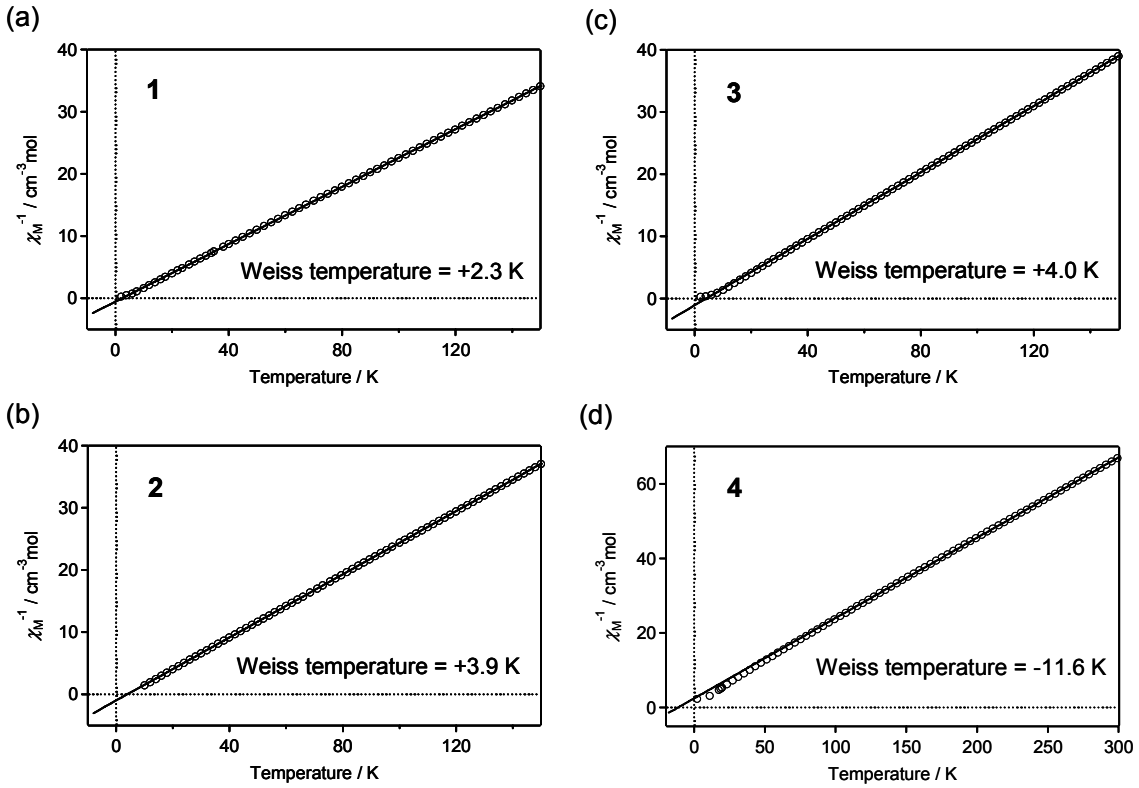

Fig. S3 The observed χ_M^{-1}–T plots for **1** (a), **2** (b), **3** (c), and **4** (d). The data between 100 and 150 K for **1**, **2** and **3**, and the data between 100 and 300 K for **4** at a cooling rate of –0.5 K/min are fitted to Curie-Weiss plots (–).

Magnetic property for 4:

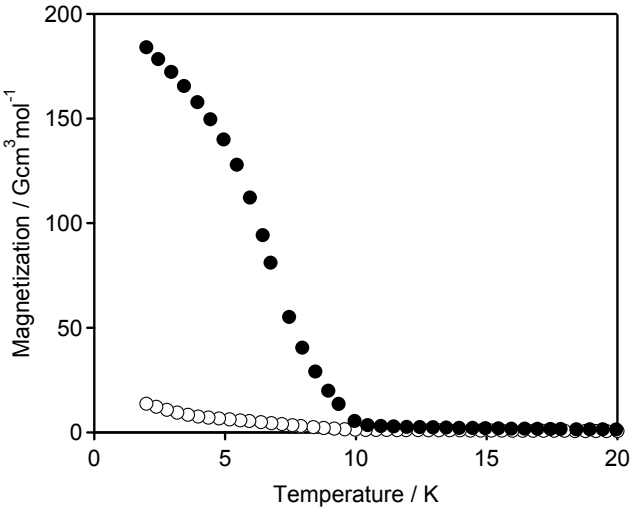

Fig. S4 Field-cooled magnetization (FCM) obtained as the temperature decreases in an external magnetic field of 10 G for **4**: (○) HT phase at a cooling rate of –0.5 K/min; (●) LT phase at a cooling rate of –0.01 K/min.