Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Investigation of Highly Ferromagnetic Mn_2Ge_4 and Mn_2Ge_5 Clusters via Photoelectron Spectroscopy and Theoretical Calculations

Li-Juan Zhao,[ab] Hong-Guang Xu,[ab] Xi-Ling Xu,[ab] and Wei-Jun Zheng*[ab]*

[a] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail: xuhong@iccas.ac.cn; zhengwj@iccas.ac.cn

[b] University of Chinese Academy of Sciences, Beijing 100049, China.

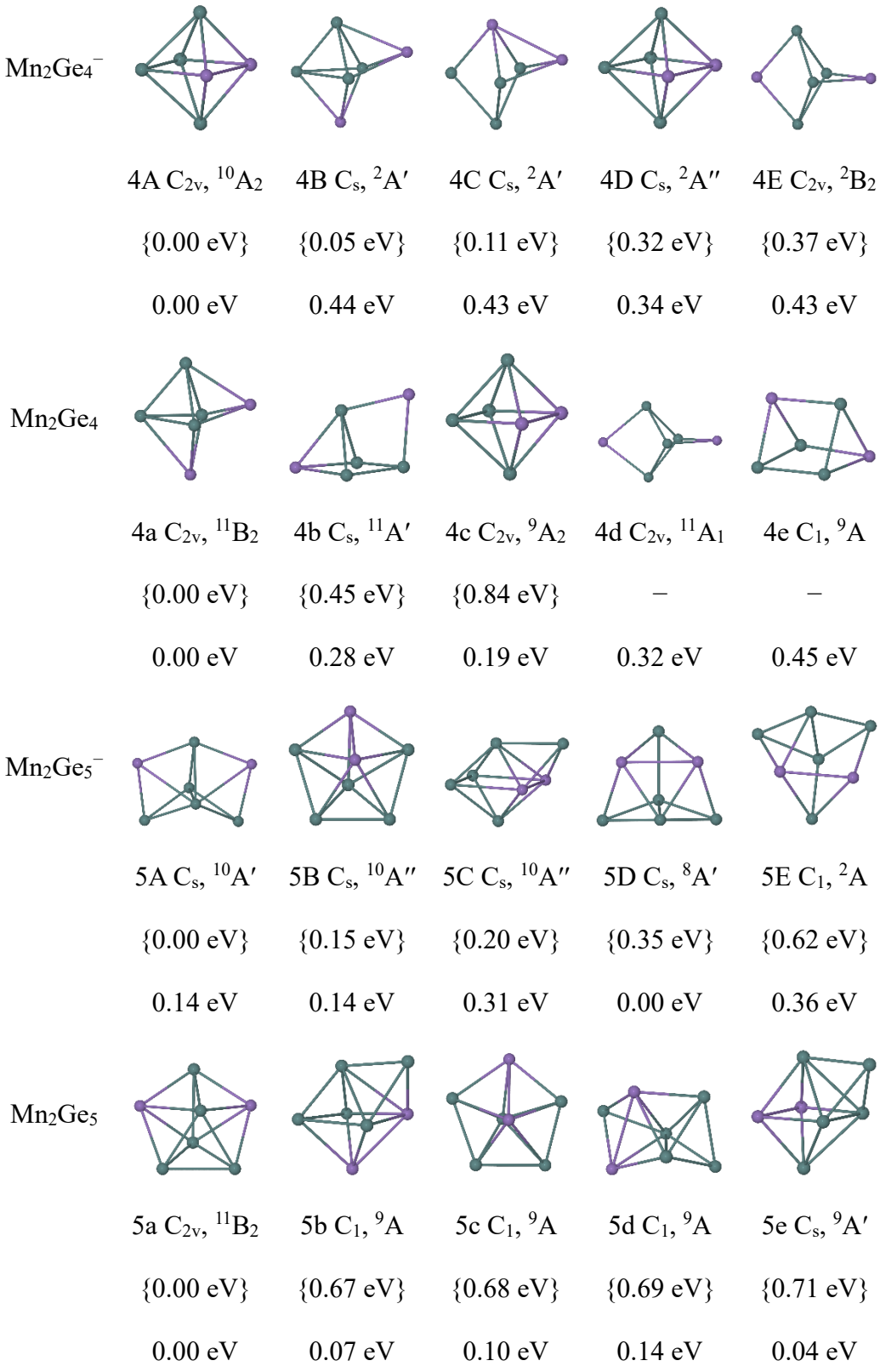

Figure S1. First five low-lying isomers of $Mn_2Ge_4^{-/0}$ and $Mn_2Ge_5^{-/0}$ optimized at the B3LYP/def2-TZVP level. The point group, electronic state, and the relative energies (in eV) are also given. The relative energies at the CCSD(T) level are shown in curly brackets.

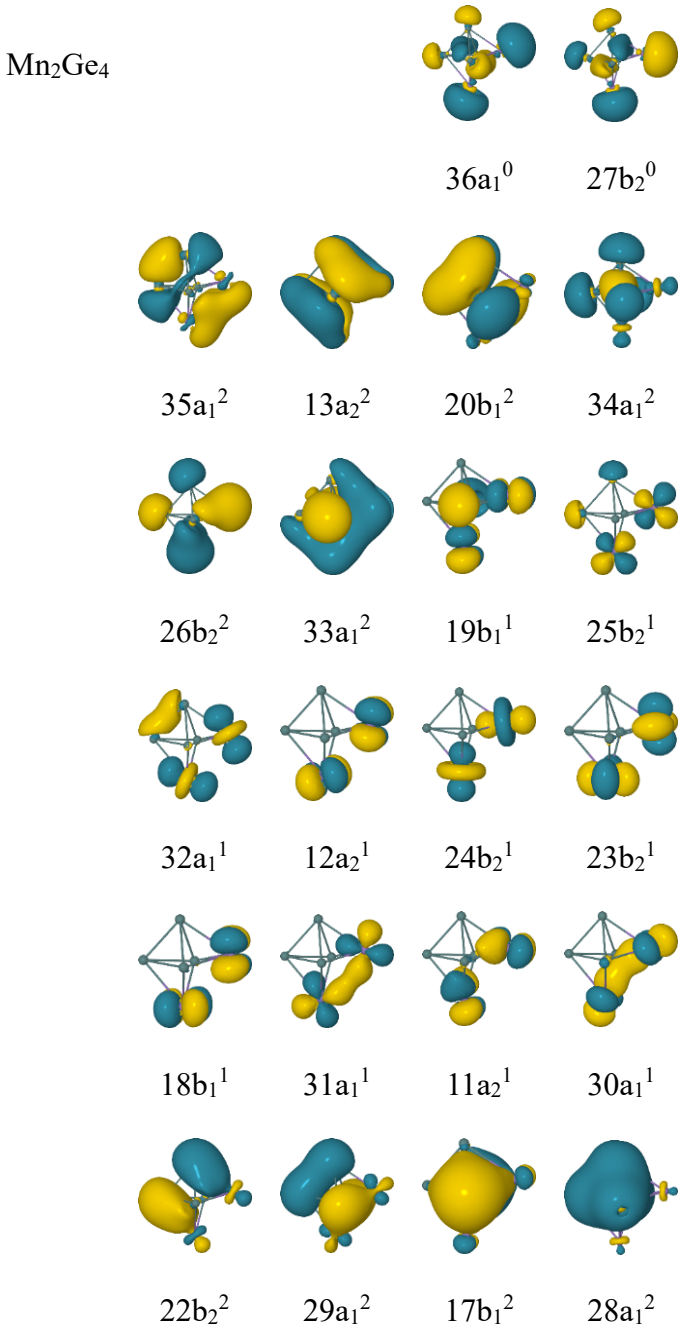

Figure S2. The canonical molecular orbitals of Mn_2Ge_4 at the B3LYP/def2-TZVP level. The contour values are ± 0.03 a.u.

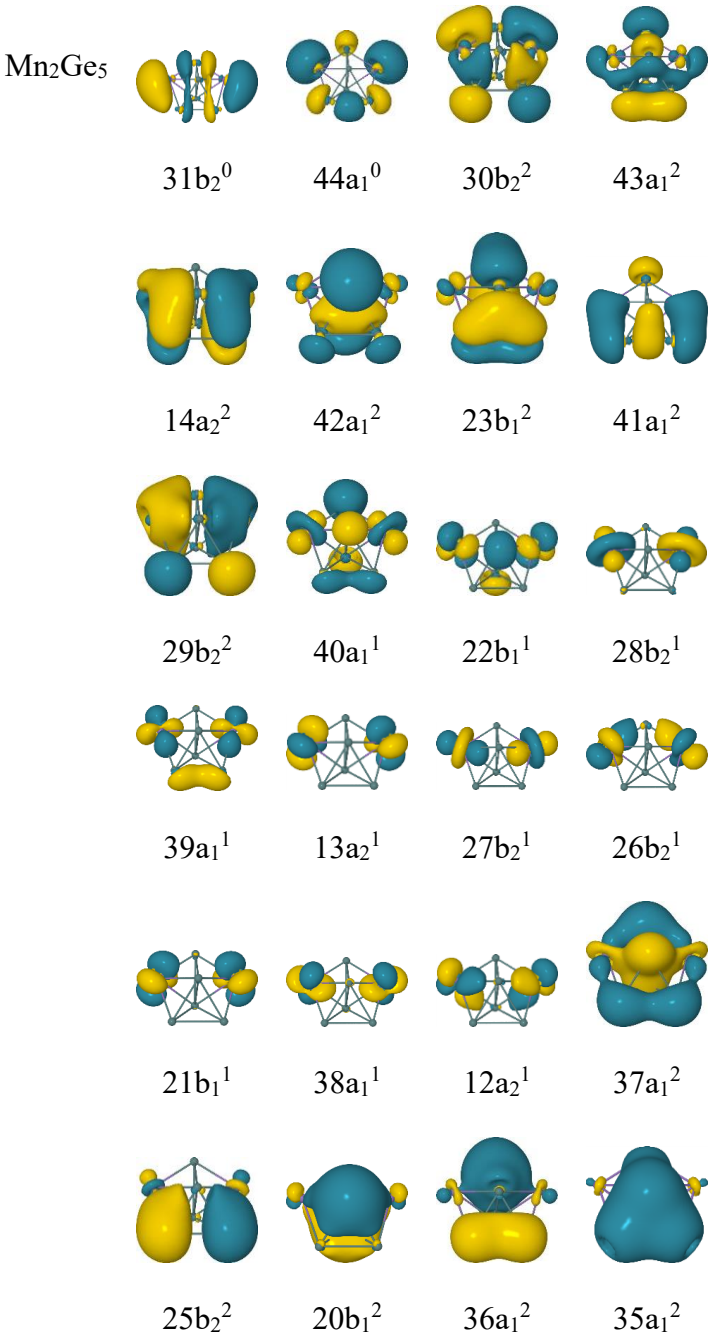

Figure S3. The canonical molecular orbitals of Mn_2Ge_5 at the B3LYP/def2-TZVP level. The contour values are ± 0.03 a.u.

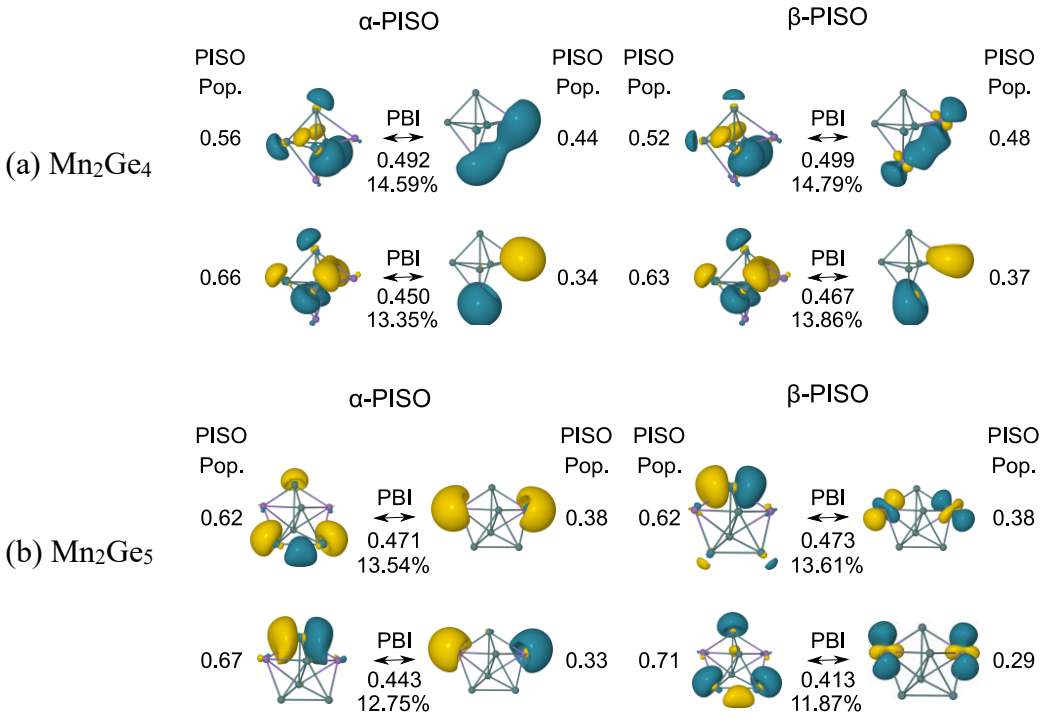

Figure S4. PISO analyses of (a) Mn_2Ge_4 with Ge_4 and Mn_2 as two fragments and (b) Mn_2Ge_5 with Ge_5 and Mn_2 as two fragments based on the B3LYP/def2-TZVP calculations. The contour values are ± 0.05 a.u.

Table S1. The calculated relative energies (R.E., in eV) and ADE/VDE values (in eV) of the first five low-lying isomers of $Mn_2Ge_4^-$.

Anions	CCSD(T)		B3LYP	
	R.E. (eV)	ADE/VDE (eV)	R.E. (eV)	ADE/VDE (eV)
$Mn_2Ge_4^-$ 4A	0.00	1.73/2.70	0.00	2.07/2.38
$Mn_2Ge_4^-$ 4B	0.05	1.69/2.01	0.44	1.63/1.80
$Mn_2Ge_4^-$ 4C	0.11	1.62/2.04	0.43	1.63/1.92
$Mn_2Ge_4^-$ 4D	0.32	1.41/2.03	0.34	1.73/2.05
$Mn_2Ge_4^-$ 4E	0.37	1.73/2.34	0.43	1.96/2.40

Table S2. The calculated relative energies (R.E., in eV) and ADE/VDE values (in eV) of the first five low-lying isomers of $Mn_2Ge_5^-$.

Anions	CCSD(T)		B3LYP	
	R.E. (eV)	ADE/VDE (eV)	R.E. (eV)	ADE/VDE (eV)
$Mn_2Ge_5^-$ 5A	0.00	2.12/2.44	0.14	2.25/2.34
$Mn_2Ge_5^-$ 5B	0.15	1.99/2.28	0.14	2.19/2.21
$Mn_2Ge_5^-$ 5C	0.20	1.39/2.28	0.31	1.72/2.11
$Mn_2Ge_5^-$ 5D	0.35	1.24/2.29	0.00	2.02/2.42
$Mn_2Ge_5^-$ 5E	0.62	1.79/2.21	0.36	1.86/2.31

Table S3. Theoretical VDEs of $Mn_2Ge_5^-$ (5B) obtained with the TD-B3LYP methods. The VDE_1' value is shifted to align with the one at the CCSD(T) level.

	Final state	Final electronic configuration	VDE (eV) (theor.)
$Mn_2Ge_5^-$ 5B	$^9A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{2}65a′^{2}44a″^{2}66a′^{1}	2.28
	$^9A'$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{2}65a′^{2}44a″^{1}66a′^{2}	2.60
	$^{11}A'$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{2}65a′^{2}44a″^{1}66a′^{2}	2.94
	$^9A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{2}65a′^{1}44a″^{2}66a′^{2}	3.03
	$^{11}A'$	…40a″^{1}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{2}65a′^{2}44a″^{2}66a′^{2}	3.13
	$^{11}A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{2}65a′^{1}44a″^{2}66a′^{2}	3.25
	$^9A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{1}65a′^{2}44a″^{2}66a′^{2}	3.40
	$^9A'$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{1}64a′^{2}65a′^{2}44a″^{2}66a′^{2}	3.55
	$^{11}A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{2}64a′^{1}65a′^{2}44a″^{2}66a′^{2}	3.59
	$^{11}A'$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{2}43a″^{1}64a′^{2}65a′^{2}44a″^{2}66a′^{2}	3.79
	$^9A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{1}43a″^{2}64a′^{2}65a′^{2}44a″^{2}66a′^{2}	4.19
	$^{11}A''$	…40a″^{2}41a″^{1}61a′^{1}42a″^{1}62a′^{2}63a′^{1}43a″^{2}64a′^{2}65a′^{2}44a″^{2}66a′^{2}	4.42

Table S4. Calculated natural charges of $Mn_2Ge_4^{-/0}$ and $Mn_2Ge_5^{-/0}$ at the B3LYP/def2-TZVP level.

$Mn_2Ge_4^-$	natural charge	Mn_2Ge_4	natural charge
Ge1	-0.38	Ge1	-0.20
Ge2	-0.38	Ge2	-0.20
Ge3	-0.63	Ge3	-0.59
Ge4	-0.63	Ge4	-0.59
Mn5	0.51	Mn5	0.79
Mn6	0.51	Mn6	0.79
$Mn_2Ge_5^-$	natural charge	Mn_2Ge_5	natural charge
Ge1	-0.28	Ge1	-0.15
Ge2	-0.28	Ge2	-0.15
Ge3	-0.30	Ge3	-0.50
Ge4	-0.50	Ge4	-0.50
Ge5	-0.70	Ge5	-0.50
Mn6	0.53	Mn6	0.90
Mn7	0.53	Mn7	0.90