Electronic Supporting Information

Magnetism of single-doped paramagnetic tin clusters studied by temperature-dependent enhanced Stern-Gerlach experiments: Impact of the diamagnetic ligand field and paramagnetic dopant

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1 Quantitative determination of Zero-Field Splitting in $Sn_{14}Mn$

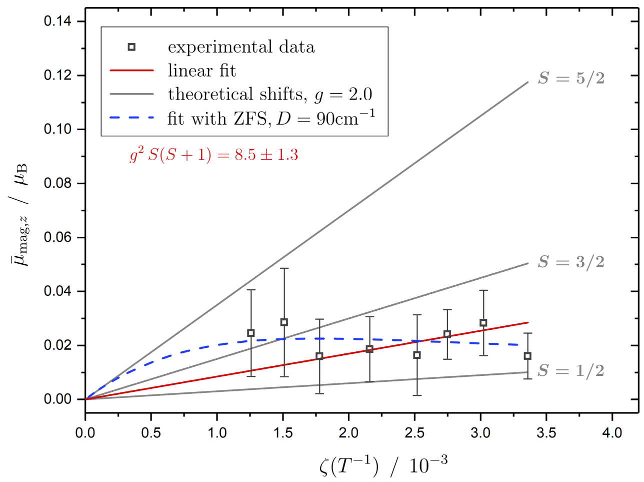

Figure S1. Temperature-dependent shift (black squares) for $Sn_{14}Mn$ as shown in the main work. A linear function (red solid line) is fitted to the temperature-dependent shifts to determine the magnetic properties in combination with the theoretical shifts for different multiplicities S and $g = 2$ (grey solid line). In the left upper corner of the Curie plots, the resulting slope of each linear fit function is listed. Here, the deviation from the Curie behaviour is additionally fitted as a blue dashed line by considering the temperature-dependent population of the $|M_S|$ states. Assuming a multiplicity of $S = 5/2$ and $g = 2.0$, a zero-field splitting constant of $D = 90$ cm^{-1} results.

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2 Composition of the Molecular Orbitals

Table S1. Composition of the molecular orbitals of Sn_{14}TM (TM = Cr, Mn, Fe) near the electron gap. Here, only the shares of the TMs atomic orbitals are shown with a threshold of 10 %. Additionally, the lowest-unoccupied (LUMO), the highet-occupied (HOMO) and the single-occupied molecular orbitals (SOMO) are indicated.

MO	Sn14Cr Cr	Sn14Mn Mn	Sn14Fe Fe
150	$5s$, $6s$, $3s$, $4s$	$5s$, $4s$, $3s$, $6s$, $3d_{x^2-y^2}$	$5s$, $3d_{xy}$, $4d_{xy}$, $6s$, $4s$, $3s$, $3d_{xy}$
151	–	$3d_{z^2}$, $4d_{z^2}$, $3d_{x^2-y^2}$, $5d_{z^2}$, $4d_{x^2-y^2}$	$3d_{z^2}$, $4d_{z^2}$, $3d_{x^2-y^2}$, $5d_{z^2}$, $4d_{x^2-y^2}$, $5d_{x^2-y^2}$, $6s$
152	$5p_x$	$3d_{yz}$, $4d_{yz}$, $5d_{yz}$, $6d_{yz}$	$3d_{xy}$, $4d_{xy}$, $5d_{xy}$, $6s$, $5s$, $3d_{z^2}$
153	–	$3d_{x^2-y^2}$, $4d_{x^2-y^2}$, $3d_{z^2}$, $5d_{x^2-y^2}$, $4d_{z^2}$, $5s$, $5d_{z^2}$	$3d_{yz}$, $4d_{yz}$, $5d_{yz}$, $3d_{xz}$, $4d_{xz}$
154	$5p_y$	$5p_x$	$3d_{xz}$, $4d_{xz}$, $3d_{yz}$, $5d_{xz}$, $4d_{yz}$, $5d_{yz}$
155	–	$3d_{z^2}$, $4d_{z^2}$, $5d_{z^2}$	$3d_{x^2-y^2}$, $4d_{x^2-y^2}$, $5d_{x^2-y^2}$
156	$5p_y$	$3d_{xz}$, $4d_{xz}$, $5d_{xz}$, $6d_{xz}$	$3d_{xz}$, $4d_{xz}$
157	$5p_z$, $3d_{z^2}$, $3d_{x^2-y^2}$	$3d_{xy}$, $4d_{xy}$, $5d_{xy}$, $6d_{xy}$	$3d_{z^2}$, $3d_{x^2-y^2}$, $4d_{z^2}$, $4d_{x^2-y^2}$, $5d_{x^2-y^2}$, $5d_{z^2}$
158	$5p_x$	$5p_y$, $3d_{yz}$	$3d_{xy}$
159	$5p_z$, $3d_{x^2-y^2}$, $3d_{z^2}$, $6s$	$3d_{x^2-y^2}$, $4d_{z^2}$	–
160	$3d_{yz}$, $6d_{yz}$, $4d_{yz}$, $5d_{yz}$	–	$3d_{xz}$
161	$3d_{xy}$, $4d_{xy}$, $6d_{xy}$, $5d_{xy}$	$5p_y$, $3d_{yz}$	$3d_{xy}$
162	$3d_{xz}$, $4d_{xz}$, $5d_{xz}$, $6d_{xz}$	$5p_z$, $2p_z$	$5p_z$, $6s$
163	$3d_{z^2}$, $3d_{x^2-y^2}$, $4d_{z^2}$, $5d_{z^2}$, $4d_{x^2-y^2}$, $5s$, $6d_{z^2}$, $5d_{x^2-y^2}$	$5p_x$	$5p_y$
164	$3d_{xy}$, $4d_{xy}$, $6d_{xy}$, $5d_{xy}$	–	–
165	$3d_{xz}$, $4d_{xz}$, $5p_x$, $5d_{xz}$	$5p_x$	–
166	[HOMO] $3d_{yz}$, $4d_{yz}$, $6d_{yz}$, $5d_{yz}$	–	[SOMO] $6s$, $3d_{xy}$, $3d_{z^2}$
167	[LUMO] $3d_{z^2}$, $3d_{x^2-y^2}$, $4d_{z^2}$, $4d_{x^2-y^2}$, $5d_{z^2}$, $5d_{x^2-y^2}$, $6s$	[SOMO] $3d_{x^2-y^2}$, $6s$, $3d_{z^2}$, $4d_{x^2-y^2}$	$3d_{yz}$
168	$6s$, $3d_{x^2-y^2}$, $3d_{z^2}$, $4d_{x^2-y^2}$, $5d_{x^2-y^2}$, $4d_{z^2}$, $5d_{z^2}$	[LUMO] $6s$, $3d_{z^2}$, $3d_{x^2-y^2}$	[SOMO] $6s$, d_{z^2}, $3d_{xy}$
169	$3d_{yz}$, $4d_{yz}$, $5d_{yz}$	$3d_{yz}$, $4d_{yz}$	[LUMO] $3d_{yz}$
170	$3d_{xz}$, $4d_{xz}$, $5d_{xz}$	$3d_{xz}$, $4d_{xz}$	–
171	$3d_{xy}$, $4d_{xy}$, $5d_{xy}$	$3d_{xy}$, $4d_{xy}$	$6s$, $3d_{x^2-y^2}$
172	$3d_{yz}$, $5p_y$	$5p_y$	–
173	$3d_{xz}$	–	$6s$, $3d_{x^2-y^2}$
174	$6s$, $3d_{x^2-y^2}$	$6s$	$3d_{xz}$, $5p_x$
175	$6s$, $3d_{z^2}$, $5s$, $3d_{x^2-y^2}$	$6s$, $5s$, $3d_{z^2}$	$6s$, $5s$, $4s$