Supplementary information for Magnetic dipolar ordering and quantum phase transition in Fe_8 molecular magnet

E. Burzurí,[1] F. Luis,[1] B. Barbara,[2] R. Ballou,[2] E. Ressouche,[3] O. Montero,[1] J. Campo,[1] and S. Maegawa[4]

[1] *Instituto de Ciencia de Materiales de Aragón, C.S.I.C. - Universidad de Zaragoza, and Dpto. de Física de la Materia Condensada, Universidad de Zaragoza, E-50009 Zaragoza, Spain*

[2] *Institut Néel, CNRS & Université Joseph Fourier, BP166, 38042 Grenoble Cedex 9, France*

[3] *CEA/Grenoble, INAC/SPSMS-MDN,17 rue des Martyrs, 38054 Grenoble Cedex 9, France*

[4] *Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan*

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I. ALIGNMENT OF THE DC MAGNETIC FIELD

The alignment method was based on the measurement of the linear longitudinal susceptibility $\chi_{zz} \equiv \partial M_z/\partial h_z$, i.e. the linear response to an oscillatory excitation magnetic field $h_z = h_0 cos(\omega t)$ applied along the easy axis z of Fe_8. This magnitude strongly depends on the orientation of the external dc magnetic field $\overrightarrow{H}$ with respect to the anisotropy axes, which we denote by z (easy axis), y (medium axis) and x (hard axis). In thermal equilibrium, the application of $\overrightarrow{H}$ along z induces a fast saturation of M_z, which therefore effectively suppresses χ_{zz}. By contrast, a transverse magnetic field (i.e. applied in the xy plane) does not break the degeneracy of spin up and spin down states. For finite field strengths ($\mu_0 H \geqslant 0.1$ T in the present experiments), the susceptibility becomes therefore *minimum* when $\overrightarrow{H}$ lies closest to the easy axis and *maximum*, when it is perpendicular to it.

In our experiments, we applied $\overrightarrow{H}$ with a 9 T × 1 T × 1 T superconducting vector magnet, which enables us to rotate $\overrightarrow{H}$ with an accuracy better than 0.001°. We hereafter denote by Z the axis of the vertical 9 T magnet and by X and Y the axes of the two horizontal 1 T magnets. The polar coordinates of the magnetic field vector in these three mutually orthogonal axes are denoted by Θ_H and Φ_H. A series of experiments were performed by recording χ_{zz} while sweeping either Φ_H (at constant Θ_H) or Θ_H (at constant Φ_H). Two representative examples, measured at $T = 4.2$ K, that is, well above the blocking temperature, are shown in Fig. 1.

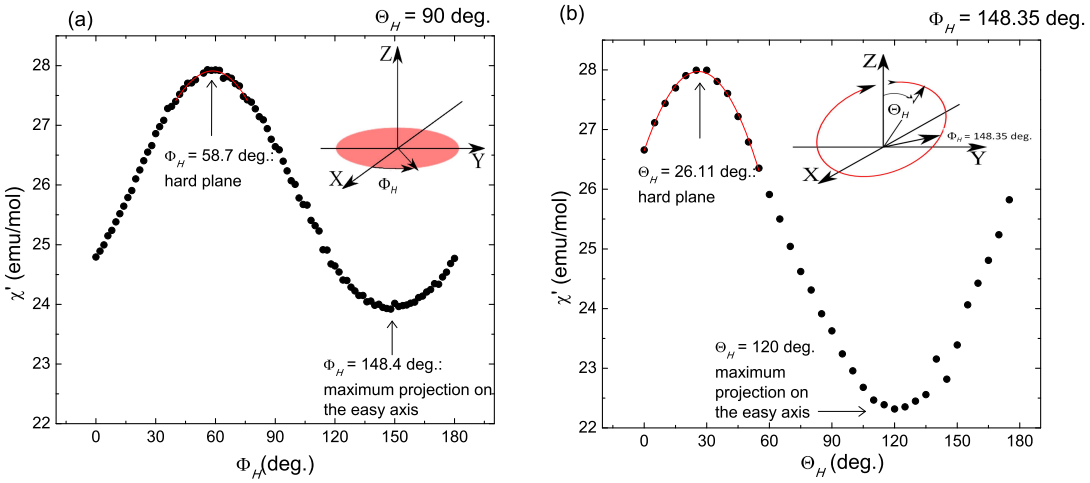

FIG. 1: Dependence of the in-phase linear susceptibility χ' of an Fe_8 single crystal, measured at $T = 4.2$ K and $\omega/2\pi = 1333$ Hz, on the orientation of an applied magnetic field of magnitude $\mu_0 H = 0.1$ T. The angles Θ_H and Φ_H refer to the coordinate axes of the vector magnet (X, Y and Z, as shown in the insets). (a) χ' *vs* Φ_H for $\Theta_H = 90$ degrees; (b) χ' *vs* Θ_H for $\Phi_H = 148.35$ degrees.

An even more precise alignment of $\overrightarrow{H}$ can be achieved by measuring the non-equilibrium, that is, the frequency-dependent susceptibility. This can be done by either increasing frequency, at fixed temperature, or by decreasing temperature at a given frequency. Figure 2 shows an example of the latter situation. Quantum tunneling and spin-lattice relaxation rates are strongly sensitive to the presence of a bias magnetic field along z. As a result, χ' shows

narrow maxima (marked by labels (a) and (c) in Fig. 2) for those H_z values that set resonant conditions between spin-down and spin-up states [1]. The largest susceptibility maximum corresponds to the condition $H_z = 0$. Using this resonance, it is possible to align $\overrightarrow{H}$ perpendicular to z within ± 0.1 degrees.

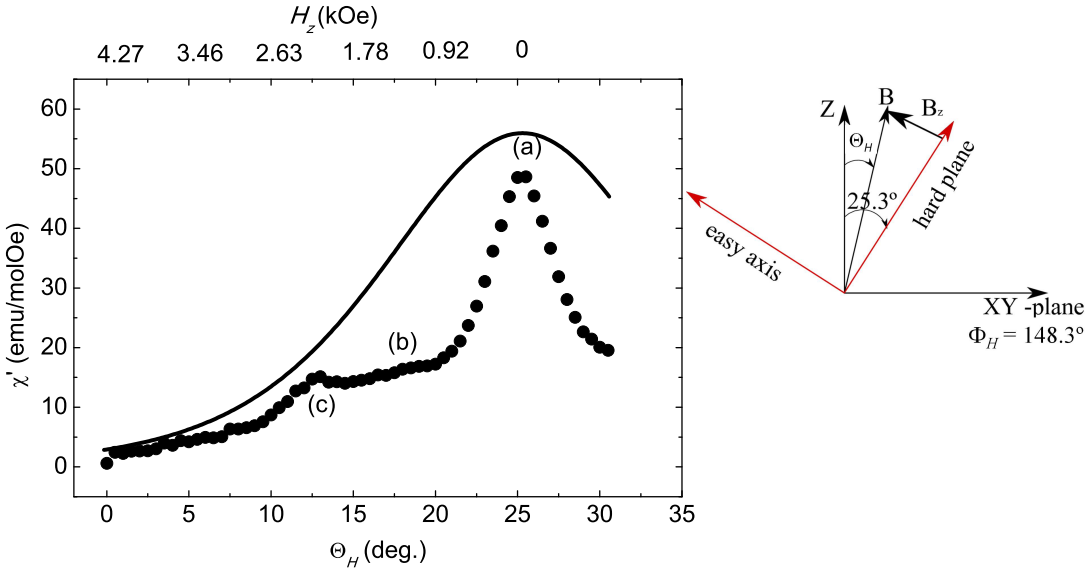

FIG. 2: •, dependence of the in-phase linear susceptibility χ' of an Fe_8 single crystal, measured at $T = 2.6$ K, on the orientation of an applied magnetic field of magnitude $\mu_0 H = 1$ T; the solid line is the equilibrium χ_{zz} at the same temperature. The experiments were performed by varying Θ_H while keeping $\Phi_H = 148.35$ degrees.

The magnetic field orientations that give χ_{zz} maxima are vectors of the xy hard magnetic plane. By recording maxima obtained in different experiments (i.e. for different fixed Θ_H or Φ_H values), it is possible to trace the magnetic anisotropy within this plane. The orientation of the magnetic field was set to maximize χ_{zz}, a condition that corresponds to the medium axis y. However, the experimental uncertainties are comparable to the variations of the susceptibility maxima. Therefore, we estimate that the magnetic field was aligned close to y, with an uncertainty close to ± 20 degrees.

All field and temperature dependent susceptibility experiments were performed at $\Theta_H = 116.5$ deg. and $\Phi_H = 6.9$ deg., for which $\overrightarrow{H}$ lies on the hard magnetic anisotropy plane, close to the medium axis (i.e., $\theta = 90$ deg. and $\phi \simeq 68$ deg., as discussed in the main text).

Because of the strong magnetic anisotropy of Fe_8, the transverse magnetic field exerts a large torque on the crystal. In order to prevent it from moving, the crystal was completely covered by a nonmagnetic epoxy. The stability of the crystal orientation can be checked by comparing the results of angle-dependent experiments performed before and after the field-dependent measurements. An example is given in Fig. 3. Both experimental curves, separated in time by more than 10 days in which magnetic field and temperature were repeatedly swept back and forth, show maxima at $\Phi_H \simeq 6.9$ degrees.

II. EFFECT OF QUANTUM FLUCTUATIONS ON THE PARAMAGNETIC SUSCEPTIBILITY

Figure 1 of the main text shows that the paramagnetic susceptibility, that is, above T_c, decreases by increasing $H_\perp$. As we argue next, this decrease results from the perturbation of the energy eigenstates $|n\rangle$ of Fe_8 by the transverse field. The Hamiltonian of an isolated Fe_8 cluster reads as follows

$$\mathcal{H}_0 = -DS_z^2 + E\left(S_x^2 - S_y^2\right) - g\mu_B\left[H_\perp(S_x\cos\phi + S_y\sin\phi) + H_z S_z\right] \quad (1)$$

with $S = 10$, $D/k_B = 0.294$ K, $E/k_B = 0.046$ K, and $g = 2$. Here, angle ϕ refers to the magnetic field orientation with respect to the local magnetic axes (x and y) of Fe_8. The susceptibility χ_{zz} can be calculated then as the sum of two terms

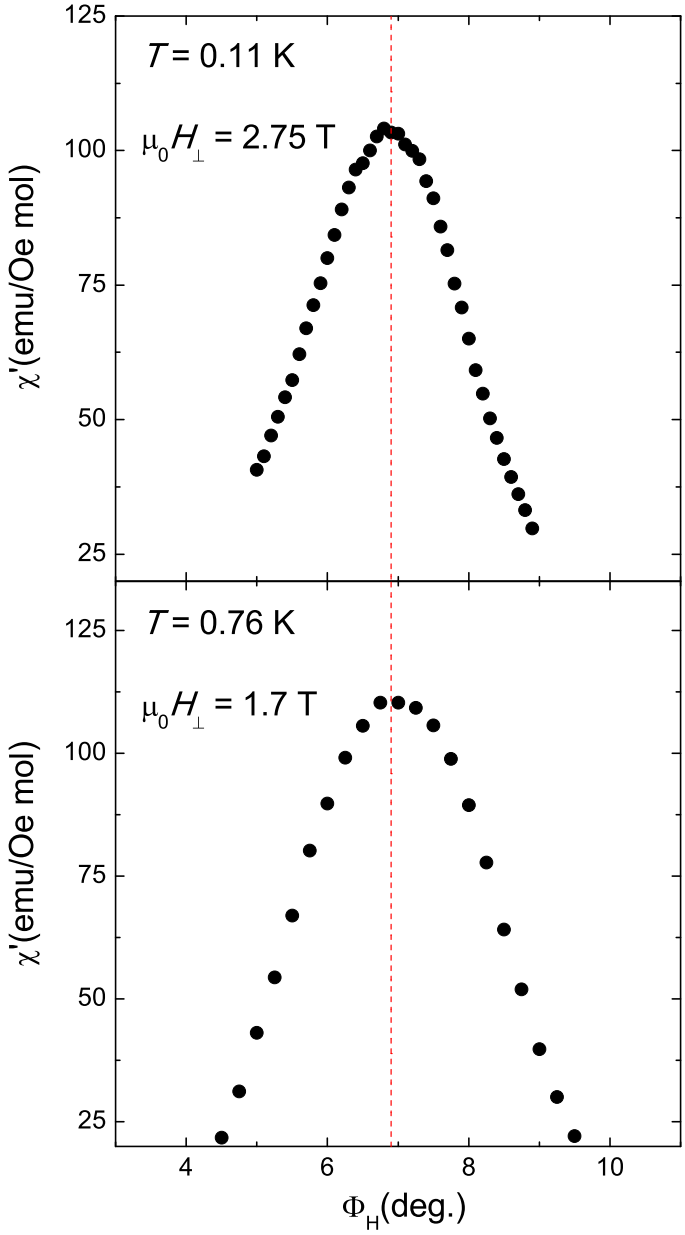

FIG. 3: Dependence of the in-phase linear susceptibility χ' of an Fe_8 single crystal on the orientation of the applied magnetic field. In these experiments, Φ_H was scanned and $\Theta_H = 116.5$ deg. The maximum susceptibility, at $\Phi_H = 6.9$ deg., occurs when the magnetic field lies on the hard magnetic anisotropy plane, close to the medium axis ($\phi \simeq 68$ deg., as discussed in the main text). Top panel: measurements performed at $T = 0.11$ K and for $\mu_0 H = 2.75$ T. Bottom panel: measurements performed at $T = 0.76$ K and for $\mu_0 H = 1.7$ T. The former experiments were carried out ten days after the latter. Between these two, all the field-dependent experiments shown in Figs. 1-3 of the main text were performed at a fixed $\Phi_H = 6.9$ deg. (vertical dotted line).

$$\chi_{zz} = \chi_{\rm th} + \chi_{\rm vv} \tag{2}$$

The first of these arises from thermal fluctuations of S_z. The latter is the van Vleck susceptibility, which reflects changes in the energy wavefunctions $\langle m|n\rangle$ induced by the excitation magnetic field h_z. Here, $\{|m\rangle\}$ denotes the basis of eigenstates of S_z, with eigenvalues $-S \leqslant m \leqslant +S$. $\chi_{\rm th}$ and $\chi_{\rm vv}$ can be easily calculated using the eigenstates $|n\rangle$ and eigenvalues E_n of the spin Hamiltonian, as follows:

$$\chi_{\rm th} = N_{\rm A}\frac{(g\mu_{\rm B})^2}{k_{\rm B}T}\left(\langle S_z^2\rangle_T - \langle S_z\rangle_T^2\right) \tag{3}$$

where

$$\langle S_z^2\rangle_T = \frac{1}{Z}\sum_n \langle n|S_z|n\rangle^2 \exp\left(-E_n/k_{\rm B}T\right), \tag{4}$$

and

$$\langle S_z\rangle_T = \frac{1}{Z}\sum_n \langle n|S_z|n\rangle \exp\left(-E_n/k_{\rm B}T\right), \tag{5}$$

while

$$\chi_{\rm vv} \simeq N_{\rm A}\frac{2(g\mu_{\rm B})^2}{Z}\sum_n\left[\sum_{n'\neq n}\frac{|\ \langle n|S_z|n'\rangle\ |^2}{E_{n'}-E_n}\right]\exp\left(-E_n/k_{\rm B}T\right) \tag{6}$$

and Z is the partition function. In thermal equilibrium, $\chi_{\rm th}$ becomes the dominant contribution to χ_{zz}.

In the paramagnetic phase, dipolar interactions between Fe_8 spins in the crystal give rise to a nearly Gaussian distribution of bias magnetic fields H_z [2]. A typical dipolar H_z can be estimated using the condition $2g\mu_B H_z S \simeq k_{\rm B}T_{\rm c}$, where $T_{\rm c} = 0.6$ K is the Curie temperature. This gives $H_z \simeq 200$ Oe. For $H_\perp = 0$, the tunnel splitting of the ground state $\Delta_S/k_{\rm B} \sim 10^{-7}$ K, that is, much smaller than the typical dipolar bias ($\sim k_{\rm B}T_{\rm c}$). Under these conditions, the two low-lying eigenstates of Fe_8 (with $n = 1$ and 2) are approximate eigenstates of S_z, with eigenvalues $m = \pm S$. The average $\langle S_z^2\rangle_T$ attains then its maximum value ($\simeq S^2$), which according to Eqs. (2), (3), and (4) is directly reflected in the paramagnetic χ_{zz}.

When $H_\perp \neq 0$, the second and third terms in (1) mix $|m\rangle$ and $|m \pm 1\rangle$ states. As a result, the wavefunctions describing the states of the ground state doublet tend to delocalize in S_z. Therefore, $\langle S_z^2\rangle_T$ must decrease with increasing $H_\perp$. This effect is indeed confirmed by calculations of the dynamical susceptibility, results of which are shown in Fig. 4. The equilibrium susceptibility was calculated numerically using Eqs. (2), (3), (4), (5), and (6). The frequency-dependent susceptibility was calculated by numerically solving a Pauli master equation that governs the time-dependent populations of energy eigenstates $|n\rangle$ of (1). Further details on the underlying theory and the calculation methods can be found in [3–6]. The results describe well the behavior that is observed experimentally (compare with Fig. 1 of the main text): as $H_\perp$ increases, the paramagnetic χ_{zz} decreases and the superparamagnetic blocking shifts towards lower temperatures.

In a real sample, however, this effect coexists with a decrease in the ordering temperature $T_{\rm c}$, thus also in the Weiss temperature, which also affect χ_{zz}. For this reason, a more direct comparison with the theoretical predictions can be done by extracting the Curie constant, that is, the slope of $1/\chi'$ *vs* T data measured above the blocking and ordering temperatures. This quantity is shown in Fig. 5, together with the theoretical prediction that follows from Eqs. (2,4,5) for $\phi = 68$ degrees and $H_z = 200$ Oe. Theory provides a satisfactory description of the experimental data, considering the experimental uncertainties. This agreement clearly shows that field-induced quantum fluctuations have important effects already at relatively high temperatures, well above $T_{\rm c}$.

This effects admits also a simple interpretation within a classical picture of anisotropic spins. As $H_\perp$ increases, the molecular spins are tilted towards the field (this 'tilt' is the classical analogue to the quantum mixing of $|m\rangle$ and $|m \pm 1\rangle$ states by $H_\perp$). As a result, the component S_z, which can follow the variations of the excitation field h_z, decreases.

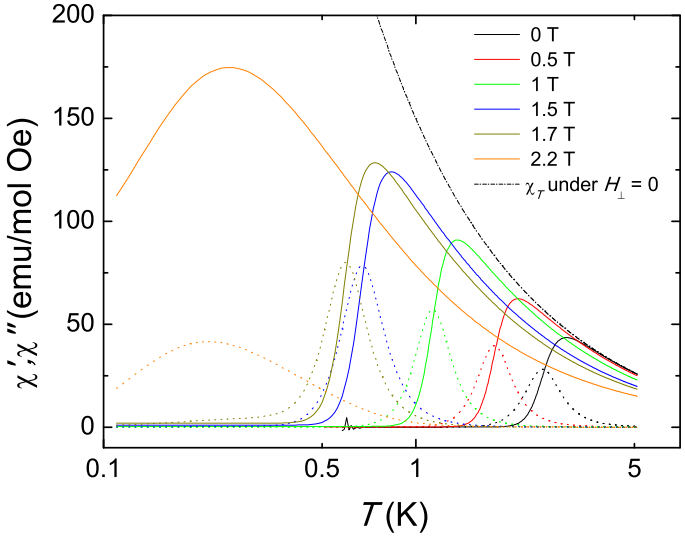

FIG. 4: Theoretical predictions for χ' (solid lines) and χ'' of Fe_8, at $\omega/2\pi = 333$ Hz and different magnitudes of the transverse magnetic field. H_z was set equal to 200 Oe, to account for the effect of the local dipolar bias fields present in the paramagnetic phase. The equilibrium χ_{zz} for $H_\perp = 0$ is also shown (dashed-dotted line).

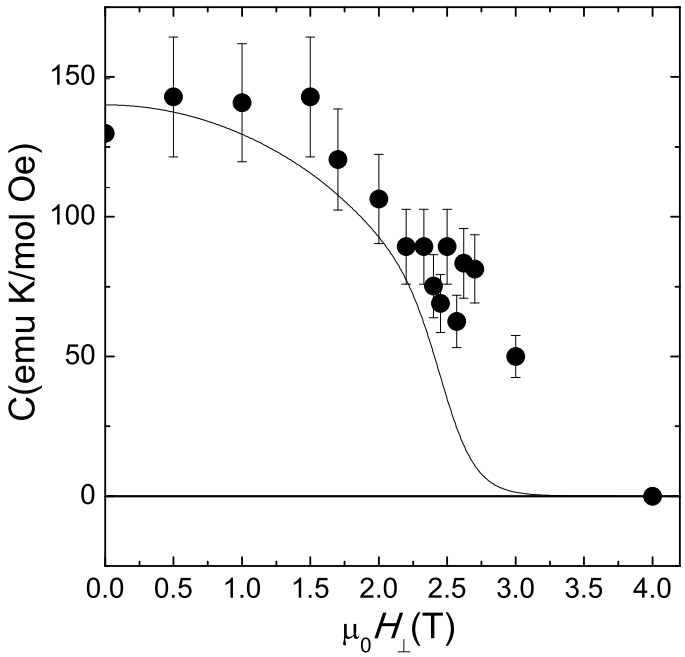

FIG. 5: Dependence of the Curie constant of Fe_8 on $H_\perp$: •, experimental data; solid line, theoretical predictions for $\phi = 68$ degrees.

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