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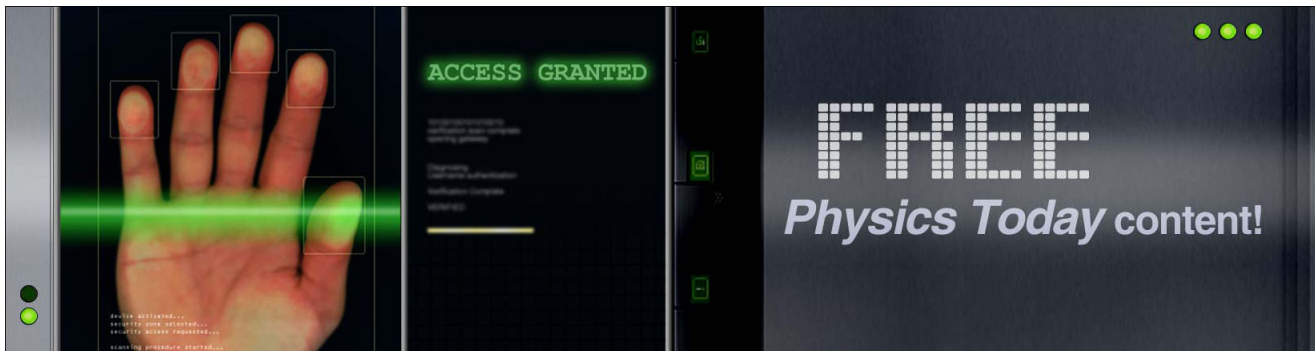
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Spin-enhanced magnetocaloric effect in molecular nanomagnets

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An unusually large magnetocaloric effect for the temperature region below 10 K is found for the Fe₁₄ molecular nanomagnet. This is to large extent caused by its extremely large spin S ground state combined with an excess of entropy arising from the presence of low-lying excited S states. We also show that the highly symmetric Fe₁₄ cluster core, resulting in small cluster magnetic anisotropy, enables the occurrence of long-range antiferromagnetic order below $T_N=1.87$ K. © 2005 American Institute of Physics. [DOI: 10.1063/1.2010604]

Nanomagnets are considered good candidates for enhanced magnetocaloric effect (MCE) at low temperatures, and therefore are of interest for applications as magnetic refrigerants in the low T range.¹ This is mostly because large magnetic moments S , resulting therefore in large magnetic entropies, are attainable in this class of materials. Large S , however, is also often associated with large particle magnetic anisotropy. The larger is the particle magnetic anisotropy, the higher is the blocking temperature and the lower is the isothermal magnetic entropy change.² Ideal materials would rather be nanomagnets with large S and small anisotropy. Opportunities are provided by molecule-based clusters, which are collections of identical nanomagnets. Recently, quantum effects were taken into account to explain the MCE of high-spin molecular clusters, such as Mn₁₂ and Fe₈,³ whereas chemical engineering was proposed to enhance MCE in Cr-based molecular rings.⁴

In this letter, we show that the Fe₁₄ molecular nanomagnet⁵ has a huge MCE in the liquid helium T region, which is much larger than that of any other known material. We show that this comes out from a combination of several features, such as the spin ground state that amounting to $S=25$ is among the highest ever reported, and the highly symmetric cluster core that results in small cluster magnetic anisotropy. The latter enables the occurrence of long-range magnetic order (LRMO) below $T_N=1.87$ K, probably of antiferromagnetic nature. We also show that low-lying excited S states additionally enhance the MCE of Fe₁₄.

Magnetization measurements down to 2 K and specific heat measurements using the relaxation method down to ≈ 0.35 K on powder samples, were carried out in a Quantum Design physical property measurement system (PPMS) setup for the $0 < H < 7$ T magnetic field range. Magnetization and susceptibility measurements below 2 K were performed using a homemade Hall microprobe appositely installed in the same setup. In this case the sample used consisted of a collection of small grains of $\sim 10^{-3}$ mm³.

The Fe₁₄ molecular cluster, nominally Fe₁₄(bta)₆O₆(OMe)₁₈Cl₆,⁵ has a highly symmetric core in which the Fe³⁺ _{$S=5/2$} spins are exchange coupled to each other by Fe-O-Fe bridges. Preliminary characterizations⁵ and simulations⁶ have shown that the Fe₁₄ molecule may have a spin ground state as large as $S=25$ and small cluster magnetic anisotropy. This is corroborated in Fig. 1 by isothermal magnetization measurements at low T .⁷ For instance, a fit of $M(H)$ data collected at $T=2$ K provides $S=25$, $g=2.06$ and uniaxial zero-field splitting as low as $D=0.04$ K. This should be considered a rough estimate of the cluster magnetic anisotropy, since, as shown below, magnetic data in the liquid helium T region are affected by low-lying excited S states.

Figure 2 shows the magnetic susceptibility $\chi(T)$ and specific heat $C(T)$ data of Fe₁₄. At first look, the main feature is given by the sharp anomaly at $T_N=(1.87\pm 0.02)$ K, that can be seen in both $\chi(T)$ and $C(T)$, and that we attribute to LRMO. The $\chi(T)$ data from ~ 10 K down to 0.35 K, taken with Hall microprobe, are properly scaled with data collected for $T > 2$ K using a calibrated magnetometer, both with applied field $H=0.01$ T. The maximum χ at T_N corresponds to ~ 56 emu/mol (Fig. 2, upper panel), which is smaller than that expected for paramagnetic $S=25$ spin. This suggests that a full ordered $S=25$ state inside the cluster is not achieved at

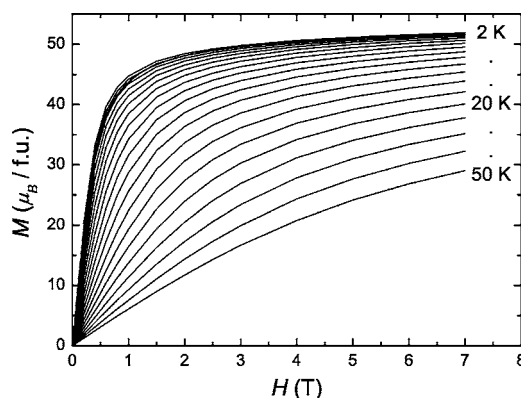


FIG. 1. Isothermal $M(H)$ curves measured at different temperatures from 2 to 50 K.

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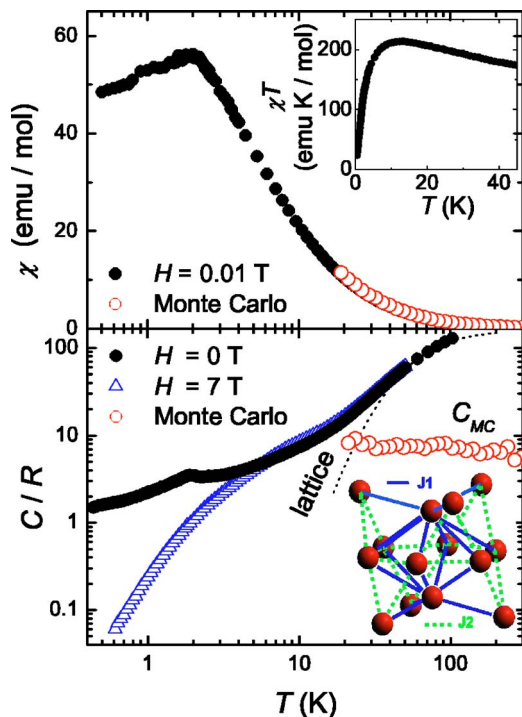


FIG. 2. (Color online) Top: $dc\text{-}\chi(T)$ [and $dc\text{-}\chi T(T)$ in the inset] taken for $H=0.01$ T. Bottom: $C(T)$ for $H=0$ and 7 T. Empty dots are Monte Carlo simulations for $H=0$. Dotted line is the lattice contribution. The sketch of the metallic core highlights the two chemically distinct exchange interactions J_1 (solid line) and J_2 (dotted line), as indicated.

T_N , likely because (i) internal degrees of freedom allow spin states other than $S=25$ to contribute, and/or (ii) inter-cluster interactions are similar in magnitude to the intra-cluster ones. The observed behavior is compatible with an antiferromagnetic nature of the ordered phase, as suggested by the sharp decrease of $\chi T(T)$ at low T (inset of Fig. 2).

The specific heat data C/R , shown in the lower panel of Fig. 2 for $H=0$ and 7 T, corroborate the interpretation of the χ data: the λ -type anomaly in the zero-field C at T_N , revealing the onset of LRMO, is quickly removed by the application of an external H , proving its magnetic origin. The occurrence of LRMO implies relatively small cluster magnetic anisotropy, otherwise superparamagnetic blocking above T_N should be observed. However, even a small anisotropy may become important for a S as large as that of Fe_{14} . This is reflected, for instance, in the relative height of the transition peak at T_N that, amounting to $\approx 1.2 R$, is apparently a bit too small for such a large S , suggesting that a large portion of the magnetic entropy is not available for the ordering mechanism. The C data measured above 20 K show a large increase, that we associate with the lattice contribution.⁸

In what follows, we evaluate the MCE for the Fe_{14} molecular compound from experimental data. This procedure includes the evaluation of the isothermal magnetic entropy change ΔS_m upon a magnetic field change ΔH , from the measured magnetization and specific heat. Moreover, we also evaluate the adiabatic temperature change ΔT_{ad} upon ΔH , from specific heat data.

In an isothermal process of magnetization, ΔS_m can be derived from Maxwell relations by integrating over the magnetic field change $\Delta H=H_f-H_i$, i.e., $\Delta S_m(T)_{\Delta H} = \int_{H_i}^{H_f} [\partial M(T, H) / \partial T]_H dH$. From $M(H)$ data of Fig. 1, the obtained $\Delta S_m(T)$ for $\Delta H=(7-0)\text{T}$ ⁹ is displayed in the upper

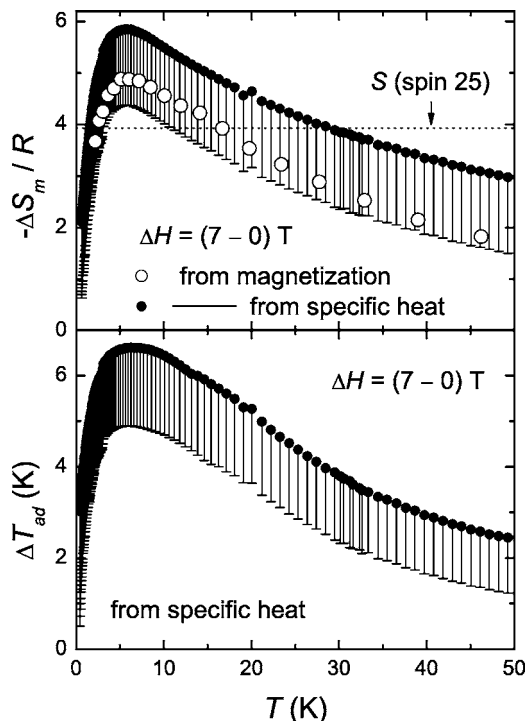


FIG. 3. Top: $\Delta S_m(T)$ as obtained from C (filled dots and bars) and M data (empty dots), both for $\Delta H=(7-0)\text{T}$. Dotted line is the limiting entropy for $S=25$. Bottom: $\Delta T_{ad}(T)$ as obtained from C data (filled dots and bars) for $\Delta H=(7-0)\text{T}$.

panel of Fig. 3. It can be seen that $-\Delta S_m(T)$ reaches a maximum of $4.9 R$ at $T=6$ K.

We next turn to the evaluation of MCE from C data of Fig. 2. We first determine the total entropies for $H=0$ and 7 T as functions of T , i.e., $S(T)_H = \int_0^T [C(T)_H / T] dT$. Experimental entropies are obtained integrating down to the lowest achieved $T \approx 0.35$ K and, obviously, not from $T=0$ K as required. To account for the lower- T region, we extrapolate linearly the experimental C below T_N for $T \rightarrow 0$ K, and calculate the associated entropy content. Successively, for $\Delta H=(7-0)\text{T}$, we calculate $\Delta S_m(T)_{\Delta H} = [S(T)_{7\text{T}} - S(T)_0]_T$ and $\Delta T_{ad}(T)_{\Delta H} = [T(S)_{7\text{T}} - T(S)_0]_S$. Note that the estimation of the lattice contribution is irrelevant for our calculations, since we deal with differences between total entropies at different H . The results obtained, considering the $T \rightarrow 0$ K extrapolation of the experimental C , are displayed in Fig. 3 as filled dots, whereas the added bars are obtained without considering this extrapolation and can be considered as a lower bound. For $\Delta H=(7-0)\text{T}$ and $T=6$ K, we get $-\Delta S_m = (5.0 \pm 0.8) R$, or equivalently $(17.6 \pm 2.8) \text{ J/Kg K}$, and $\Delta T_{ad} = (5.8 \pm 0.8) \text{ K}$. It can be noticed that, within the bars, the so-obtained ΔS_m fully agrees with the previous estimate inferred from $M(T, H)$, suggesting that both (independent) procedures can be effectively used to characterize Fe_{14} with respect to its magnetocaloric properties.

The spin value of Fe_{14} accounts only partially for the large MCE we measured. The experimental $\Delta S_m(T)$ exceeds, indeed, the entropy expected for a $S=25$ spin system, that is, $R \ln(2S+1) \approx 3.9 R$ (Fig. 3). To explain where the observed excess of magnetic entropy change comes from, we model the magnetic and thermal properties of an isolated Fe_{14} molecule in zero-applied field by classical Monte Carlo (MC) simulations using the metropolis algorithm. Following the

arguments reported in Ref. 5 on the angles of the Fe-O-Fe bridges and looking at the bottom inset of Fig. 2, two primary categories of the Fe-O-Fe bridges inside the molecule can be identified: those that connect the apical iron ions to the face cap and equatorial iron ions (whose exchange coupling we indicate as J_1), and those characterized by much smaller angles that connect all other iron ions (J_2). We consider therefore the Hamiltonian $\mathcal{H} = -\sum_{i=1,2} \sum_{(j,k)} J_{i,j,k} \mathbf{s}_i \cdot \mathbf{s}_k$, for all possible (j,k) pairs of exchange-coupled Fe^{3+} spins. Thus, we calculate $\chi(T)$ to fit the experimental data (Fig. 2), obtaining estimates for J_1 and J_2 . To avoid the influence of inter-cluster interactions and cluster anisotropy, only data for $T > 20$ K are taken into account. Assuming $g = 2.06$ as deduced from the saturation of the magnetization, the fit provides $J_1/k_B \approx -60.0$ K and $J_2/k_B \approx -25.2$ K, where the negative sign indicates that they are both antiferromagnetic. A similar analysis of $\chi(T)$ for Fe_{14} is already reported in Ref. 6. We should mention that, on basis of our MC simulations, a slight change of the J_1/J_2 ratio has a strong influence on the determination of the cluster spin, suggesting the competing nature of the exchange interactions inside the molecule. We next use the so-obtained J_i values to calculate the specific heat C_{MC} associated with internal degrees of freedom of the molecule. We obtain a relatively large contribution $C_{\text{MC}} \sim 7-9 R$ for $20 \text{ K} < T < 300 \text{ K}$ (Fig. 2), that implies the presence of excited states close in energy to the $S=25$ ground state. Likely, large C_{MC} values have to be expected in the lower- T region as far as excited states remain populated. Recalling the uncomplete achievement of the $S=25$ spin state deduced from experimental $\chi(T)$ at T_N , and on basis of our MC simulations, we identify the entropy associated with this contribution as that responsible for the observed enhancement of the MCE of Fe_{14} . Additionally, the transition to LRMO is certainly contributing as well to the MCE parameters below ~ 2 K. When LRMO occurs, the magnetization and magnetic entropy strongly varies in a narrow T range in the vicinity of the transition temperature. However, on basis of the relatively small height of the ordering peak (Fig. 2), we do not expect this contribution to be the dominant one. Indeed, no apparent anomaly is seen in the $\Delta S_m(T)$ and $\Delta T_{\text{ad}}(T)$ curves at T_N .

The values of $\Delta S_m(T)$ and $\Delta T_{\text{ad}}(T)$ obtained in Fe_{14} are exceptionally large, even more than the ones obtained with intermetallic materials known to be, so far, the best magnetic refrigerant materials in the T range below 10 K. For instance, the best representative is the recently studied¹⁰ $(\text{Dy}_x\text{Er}_{1-x})\text{Al}_2$ alloy that, for $x \geq 0.5$ concentrations, presents MCE parameters below 10 K which are at least 30% smaller than that of Fe_{14} . Among systems of superparamagnetic particles and molecular magnets, the gap is even more pronounced. For instance, because of their well-defined spin ground state in this T and H range, it is easy to show that the well known Fe_8 and Mn_{12} -ac molecular nanomagnets, i.e., cannot exceed values of $-\Delta S_m \approx 12.5$ and 11 J/Kg K , respectively, thus much smaller than that of Fe_{14} . Moreover, in these materials, as in most molecular magnets, an additional complication (with respect to MCE parameters) is added by the blocking of the cluster spins in the liquid helium T region, causing the spin-

lattice relaxation to slow down dramatically. Therefore, cluster spins tend to loose thermal contact with the lattice¹¹ resulting in lower magnetic entropies and, consequently, lower MCE parameters. Ideally, it is desirable to keep the spin-lattice relaxation at sufficiently high rates down to lowest temperatures, in order to have a more efficient material in terms of MCE. This route was already recently tried⁴ with Cr_7Cd molecular rings, that can be seen as an ordered arrangement of well-separated paramagnetic spins, having fast relaxations in the whole (experimental) T range. In terms of MCE parameters, the only limitation of this material is given by the low cluster spin value ($S=3/2$) allowing not more than $-\Delta S_m \approx 5.1 \text{ J/Kg K}$ as experimentally reported to occur for $T < 2 \text{ K}$.⁴

Summing up, the above-reported experiments show that the Fe_{14} molecular nanomagnet is unique in terms of MCE due to the combination of the following characteristics: (i) unusually large spin ground state; (ii) small cluster magnetic anisotropy; (iii) excess of entropy resulting from low-lying excited S states; (iv) long-range magnetic ordering. For these reasons, Fe_{14} has therefore high potentiality to work as a magnetic refrigerant within a temperature range below 10 K.

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⁷We should mention here that our magnetization measurements repeatedly provided results that slightly differ from what was reported in Ref. 5. This discrepancy is beyond the experimental uncertainty. We have carefully checked the validity of the results here presented and obtained on fresh samples. We stress that the saturation values of Fig. 1 do agree with $S = 25$, as expected from considerations on the intra-molecular exchange couplings (see Ref. 5).

⁸The lattice contribution above 20 K is modeled with $n=55$ optic-like modes having Einstein temperature $\theta_E=68$ K (dotted curve in Fig. 2).

⁹For practical reasons, the measurements at the lowest applied field were carried out for $H_i=10^{-3}$ T, which in our calculations was approximated to zero-applied field.

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