

Low-temperature specific heat of Fe₆ and Fe₁₀ molecular magnets

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The energy splitting of the low-lying levels has been investigated on two magnetic molecular clusters Fe₆ and Fe₁₀ by means of low-temperature zero-field specific-heat measurements. Significant deviations from the usual $C \sim T^{-2}$ law were observed above the maximum of the main Schottky anomalies as a result of non-negligible contributions from the excited spin states with $S > 1$ and the estimated lattice contributions follow a phenomenological power law $C/R \sim T^\alpha$ with $\alpha \sim 2.7$ for both these compounds. The singlet-triplet energy gaps evaluated by the Schottky anomaly, $T_0 = 19.2$ K for Fe₆ and 4.56 K for Fe₁₀, are smaller than what we can estimate by a simplified spin-Hamiltonian approach in the strong exchange approximation and using the energy levels obtained by the high-field magnetization and susceptibility measurements. This discrepancy asks for a more complex description of the low-lying states of these molecular clusters, beyond the strong exchange approximation. At very low temperatures $T \ll 1$ K, two low-energy Schottky anomalies were also observed in Fe₁₀, probably due to a small fraction of defected rings or to hyperfine contributions.

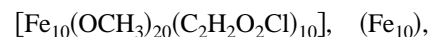
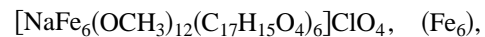
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INTRODUCTION

Mesoscopic magnetic systems have attracted much attention for several reasons, including the possibility of observing quantum phenomena on a macroscopic scale and also to observe the crossover from a genuine quantum to classical behavior. Thanks to the recent developments of synthetic chemistry, large magnetic molecules containing from 4 to 20 magnetically interacting metal ions have recently received a great deal of interest as potential single-molecule magnets.¹ The chemical approach to the synthesis of magnetic clusters embedded in a molecular crystal structure is actually one of the most promising ways to assemble mesoscopic systems and so far it has provided magnetic systems which are very appealing from several points of view. These magnetic objects are indeed strictly monodisperse and often highly symmetric and these features actually provide the opportunity to develop models of reasonable complexity. Moreover, materials can be produced in bulk quantity so that several and complementary experimental techniques can be used for their study.

Most studies have been so far focused on clusters like Mn₁₂ (Ref. 2) and Fe₈ (Ref. 3) which exhibit bistability and macroscopic quantum tunneling of the magnetization at low temperatures. Synthetic ringlike structures like Fe₆ and Fe₁₀ are also appealing as model systems due to their high symmetry and have been investigated by means of different tech-

niques, such as susceptibility,⁴ magnetization,⁵ and nuclear magnetic resonance.⁶ Fe₆ and Fe₁₀ molecular crystals, whose chemical formula is



comprise six- and ten-membered rings of iron(III) ions, respectively, in a coplanar configuration. The methoxide ligands (OCH₃) bridge neighboring metal ions and support the cyclic skeleton, which has crystallographic S_6 symmetry in Fe₆ and idealized D_{5d} symmetry in Fe₁₀. Additional bridging chloroacetate ligands are present in Fe₁₀.^{4,5}

For the understanding and the control of the magnetic properties of these systems, it is mandatory to have a good knowledge of the ground state and the interplay among different interactions acting on the metal ions of the cluster. The low-temperature physical properties of a N -membered ring can be described by the Hamiltonian:

$$\mathbf{H} = J \sum_{i=1}^N \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \sum_{i=1}^N U_i(\mathbf{S}_i) + \sum_{i \neq j}^N U_{i,j}(\mathbf{S}_i, \mathbf{S}_j) + g \mu_B \mathbf{B} \cdot \sum_{i=1}^N \mathbf{S}_i, \quad (1)$$

which includes nearest-neighbor (NN) Heisenberg interactions (first term), magnetocrystalline (single ion) anisotropies (second term), dipolar or anisotropic-exchange contributions (third term), and Zeeman interactions (fourth term).⁴ In Eq. (1), $S_{N+1}=S_1$ and higher-order terms in the spin variables have been neglected. Different approaches have been proposed to solve Hamiltonian (1) for antiferromagnetic rings such as Fe_6 and Fe_{10} . In the case of a ring of six $S_i=5/2$ spins, for example, the Heisenberg Hamiltonian matrix (46656×46656) can be block factorized by exploiting the symmetry properties of the total spin operator $\mathbf{S}=\sum_j \mathbf{S}_j$.⁴ In this way 16 matrices, with size ranging from 1×1 to 609×609 and S values ranging from 15 to 0 must be calculated and diagonalized numerically. This method eventually gives a genuine quantum description of the ground state and can be suitably extended to include non-Heisenberg contributions. A semiclassical approach, based on the instanton method, has been recently proposed⁷ and applied to clusters containing a finite number of spins, such as the Fe_6 and the Fe_{10} studied in this work.

In the case of Fe_6 and Fe_{10} clusters, NN Heisenberg interactions represent the dominant term—at least in low magnetic fields—and lead to a nonmagnetic $S=0$ ground state and a set of multiplets regularly spaced in energy. High-temperature magnetic susceptibility data recorded at 1 T on polycrystalline samples were indeed accurately fitted by a NN Heisenberg Hamiltonian with $j=20.0 \text{ cm}^{-1}$ in Fe_6 (Ref. 4) and 9.6 cm^{-1} in Fe_{10} .⁵ However, magnetic ground states can be achieved by application of a magnetic field strong enough to partially override the intermolecular antiferromagnetic ordering of the spins and at very low temperature ($T \leq 1 \text{ K}$) the magnetization shows characteristic, evenly spaced quantum steps as we discuss in Ref. 8. In that work,⁸ we show how it is possible to independently evaluate the energy gaps among multiplets and their anisotropy terms and consequently to have a “spectroscopic” description of the low-lying states from high-field magnetization experiments performed on single crystal.

The energy separation of the ground state from the excited multiplets gives rise to a Schottky anomaly in the specific heat. Differently from what is observed in most paramagnetic compounds or molecular crystals containing dimers for example,⁹ the energy gap between the ground and the first excited state in molecular clusters is of the order of 10 K, which makes these systems very appealing also for thermodynamic studies. Despite that, the large number (typically one hundred) of atoms contained in one molecule gives rise to a huge lattice contribution to the specific heat even at low temperatures. For Mn_{12} , for instance, the magnetic contribution is practically masked by the lattice specific heat¹⁰ and only the application of an external magnetic field has recently put in evidence the magnetic term.^{11,12} However, zero-field specific-heat measurements are important as they allow one to completely neglect the Zeeman energy and therefore they provide complementary information to measurements performed in a high magnetic field.

In this paper we report a study of low-temperature specific heat on Fe_6 and Fe_{10} molecular clusters. Since this experimental technique has been scarcely used so far to characterize these new molecular magnets, the aim of this work is essentially twofold: To check to which extent conventional

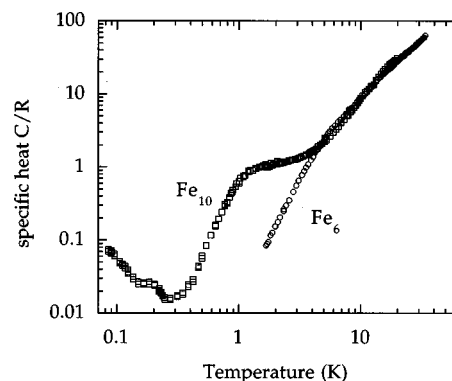


FIG. 1. Temperature dependence of the molar specific heat, in the gas constant R units, of the Fe_6 (circles) and Fe_{10} (squares) compounds.

laws such as $C/R \sim aT^{-2} + \beta T^3$, for instance, can be used to characterize the specific heat of magnetic molecular clusters and, second, to get more and complementary (with respect to measurements performed in magnetic field) information on the energy splitting of the low-lying states of Fe_6 and Fe_{10} molecular magnets.

EXPERIMENTAL DETAILS, RESULTS, AND PRELIMINARY ANALYSIS

Low-temperature heat-capacity measurements were performed at the Centre de Recherches sur les Très Basses Températures in Grenoble by means of either a continuously refilled ^4He evaporation cryostat (“1 K pot”) working between 1.6 and 30 K or a dilution refrigeration system for measurements below 1 K. In both cases the heat capacity was measured using the transient heat-pulse method.¹³ The specimen was clamped, with the help of a small quantity of Apiezon- N grease, between two Si plates on which thermometer and heater were attached and mounted on the opposite sides of the sample. In the case of the low-temperature apparatus a P-doped Si chip was used as calibrated thermometer while in the 1 K pot a Lake Shore Cernox thermometer was used. Fe_6 and Fe_{10} microcrystals were synthesized by procedures reported in the literature.^{4,5} Polycrystalline samples were pressed, without any additive (glue or Cu powder), in pellets of 8 or 12 mm diameter and with typical masses ranging between 50 and 150 mg. Our data acquisition system allows to evaluate the relaxation time τ_0 between the sample and the thermal bath and the internal relaxation time τ_1 of the sample. We continuously checked that the quasidiabatic condition $\tau_0 \gg \tau_1$ was fulfilled. The intensity of the heat pulse was chosen to obtain a temperature variation $\Delta T \leq 2\%$ of the bath temperature.

The temperature dependence of the molar specific heat C divided by the gas constant R is reported in Fig. 1 for both Fe_6 and Fe_{10} in a log-log scale. At 4 K, the C/R is close to 1 for both compounds, that is a huge value if compared with those typically observed in simple inorganic materials. The C/R vs T curves of the Fe_6 and the Fe_{10} samples are quite close to each other down to 4 K. The specific heat of Fe_6 continuously decreases down to 1.6 K, while the specific heat of Fe_{10} clearly shows a bump at $\sim 1.4 \text{ K}$ and a rapid

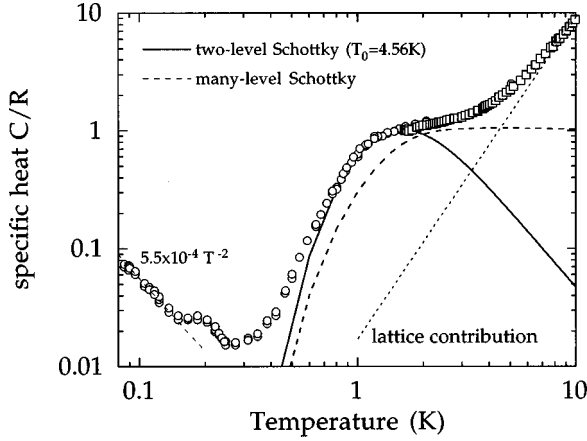


FIG. 2. Temperature dependence of the molar specific heat, in the gas constant R units, of the Fe₁₀ compound. Different symbols indicated two different experiments on two different samples. Solid line: “two-level Schottky” model with $T_0=4.56$ K. Dashed line: “many-levels Schottky” curve calculated by Eq. (3) with the multiplet levels $E(S)$ and their anisotropy splitting $D(S)$ obtained by high-field magnetization measurements (Ref. 8), namely $E_i=E(S)+D(S)[M_S^2-S(S+1)/3]$ with $S=1, \dots, 5$; $M_S=0, \pm 1, \dots, \pm S$ and $E(1)=6.445$ K, $D(1)=3.223$ K, $E(2)=18.39$ K, $D(2)=0.8619$ K, $E(3)=36.38$ K, $D(3)=0.4187$ K, $E(4)=60.41$ K, $D(4)=0.2590$ K, $E(5)=90.08$ K, $D(5)=0.1770$ K.

decrease below 1 K. A small bump and an increase of C/R are also observed at lower temperatures, i.e., $0.08 \text{ K} < T < 0.5 \text{ K}$, in this compound. We first consider in more detail the specific-heat behavior of Fe₁₀.

Two sets of data obtained on different Fe₁₀ samples and by different experimental setups are shown in Fig. 2. They nicely overlap in the 1.6–4.0 K region, showing the good reproducibility (within $\sim 6\%$) of the experiments. Preliminary information on the anomaly at 1.4 K can be obtained by fitting the raw data with a conventional two-level Schottky model:

$$C/R = \frac{g_0}{g_1} \left(\frac{T_0}{T} \right)^2 \frac{\exp(T_0/T)}{[1 + (g_0/g_1)\exp(T_0/T)]^2}, \quad (2)$$

where g_0 and g_1 are the degeneracies of the ground and the first excited state, respectively, and T_0 is the energy gap between these two states. We assume $g_0=1$ (ground state=singlet) and $g_1=3$ (first excited state=triplet). The position and the height of the bump can be nicely reproduced by Eq. (2) by adjusting only one parameter, i.e., $T_0=4.56$ K. Notice that the estimated lattice contribution, also shown in Fig. 2, is negligible for $T < 2$ K (see next paragraph for further details).

The low-temperature anomalies can be characterized by the local maximum at 0.2 K and by the increase of C/R below 0.15 K. The latter can be fitted by the $C/R=5.5 \times 10^{-4} T^{-2}$ curve, as shown in Fig. 2, which, in turn, approximates a two-level Schottky behavior for $T \gg T_0$. Thus, these low-temperature anomalies evidence the presence of two further zero-field splittings with energies typical of the hyperfine or dipole-dipole interactions (~ 0.1 K).

Differently from what is observed for Fe₁₀, the Schottky anomaly is not evident on the raw data of Fe₆ specific heat.

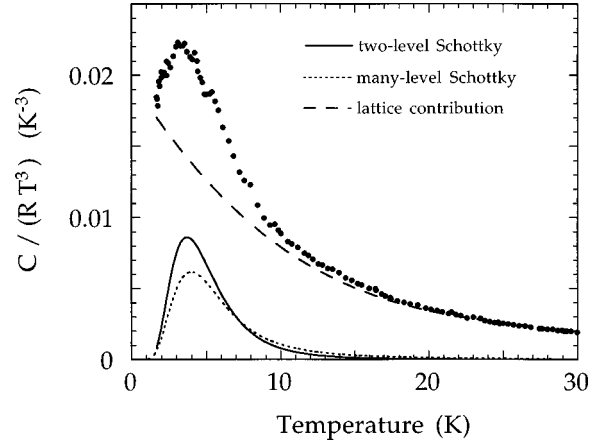


FIG. 3. A $C/(RT^3)$ vs T plot of the specific heat measured on Fe₆ compound. A bump of $C/(RT^3)$ at ~ 3.5 K is clearly visible and it can be nicely reproduced by the two-level Schottky curve with $T_0=19.2 \pm 1$ K. Dashed line: “many-level Schottky” $C/(RT^3)$ curve calculated by Eq. (3) with the multiplet levels $E(S)$ and their anisotropy splitting $D(S)$ obtained by high-field magnetization measurements (Ref. 8), namely $E_i=E(S)+D(S)[M_S^2-S(S+1)/3]$ with $S=1, \dots, 5$; $M_S=0, \pm 1, \dots, \pm S$, and $E(1)=21.99$ K, $D(1)=6.216$ K, $E(2)=65.96$ K, $D(2)=1.410$ K, $E(3)=131.93$ K, $D(3)=0.6087$ K, $E(4)=219.87$ K, $D(4)=0.3166$ K, $E(5)=329.82$ K, $D(5)=0.1770$ K.

In this case we found it more convenient to present the experimental data in a $C/(RT^3)$ vs T plot (Fig. 3), which is commonly used to show the temperature dependence of the lattice contribution in simple inorganic materials. In this kind of plot, the $C/(RT^3)$ vs T curve of Fe₆ shows an anomaly with a maximum at ~ 3.5 K and a continuous decrease of $C/(RT^3)$ above 4 K. Phonon modes with very low energy could give rise to anomalies in $C/(RT^3)$ vs T plot of data, yet a simple combination of Debye- and an Einstein-like contributions:

$$C/R = 3 \left(\frac{h\nu}{k_B T} \right)^2 \frac{\exp(h\nu/k_B T)}{[\exp(h\nu/k_B T) - 1]^2} + \beta T^3$$

does not fit the Fe₆ data at the lowest temperature, i.e., 1.6–10 K. Therefore, we can exclude a trivial lattice contribution to the specific heat with such a shape and since magnetic measurements clearly show the presence of an energy gap in this range of temperature, we are lead to consider a more realistic magnetic origin for the 3.5 K anomaly of Fig. 3. By using the simple two-level Schottky model [Eq. (2)] with $g_0=1$ and $g_1=3$, we have actually found that the position of the maximum is well reproduced by $T_0=19.2 \pm 1$ K (see Fig. 3). It should be noted, however, that the calculated magnetic contribution accounts for less than 50% of the measured specific heat, implying that the lattice and magnetic contributions have similar magnitudes in the range of liquid He temperature. In Fig. 3 we also plot, in the form C_{latt}/T^3 vs T , the lattice contribution estimated as the difference $C_{\text{latt}}=(C-C_{\text{Sch}})$ between the raw experimental data (C) and the magnetic term (C_{Sch}). It turns out that C_{latt}/T^3 decreases as the temperature increases and this implies that C_{latt} increases less rapidly than T^3 in the temperature range 1.6–30 K. A rough estimate of the Debye temperature Θ_D , from the $C_{\text{latt}}/(RT^3)$ coefficient (0.005–0.015 K⁻³), would

give Θ_D values ranging between 20 and 40 K. Since the T^3 Debye law is expected to work well only below Θ_D (typically for $T < \Theta_D/50$) it should not be surprising to find deviations from the simple T^3 Debye law. An alternative analysis of the temperature dependence of C_{latt} shows that C_{latt} vs T can be well fitted by a phenomenological power law $\Delta C/R = 0.0218 \times T^{2.64}$ in the temperature range 1.6–10 K (Fig. 4). Such an analysis is supported by the similarity of

the lattice contribution in both the Fe_6 and Fe_{10} compounds as we will further discuss in the following.

DISCUSSION

For a magnetic system with a set of energy levels E_i , the specific heat can be calculated by differentiating the total energy with respect to T , i.e., by the expression:

$$\frac{C}{R} = \beta^2 \frac{\sum_i E_i^2 \exp(-\beta E_i) \sum_i \exp(-\beta E_i) - \left[\sum_i E_i \exp(-\beta E_i) \right]^2}{\left[\sum_i \exp(-\beta E_i) \right]^2}, \quad (3)$$

where $\beta = (k_B T)^{-1}$. In the framework of a simplified spin-Hamiltonian approach and the strong exchange limit, the multiplet levels and their anisotropy splitting have been independently evaluated by high field magnetization measurements.⁸ In Fig. 3 we may compare the experimental specific-heat data of Fe_6 with the curve (named ‘‘many-level Schottky’’) calculated by Eq. (3) and the energy levels obtained by the torque experiments⁸ (see, also, the caption of Fig. 3 for further details). It turns out that the ‘‘many-level Schottky’’ curve exhibits a maximum at temperature slightly higher than the experimental one. This implies that the singlet-triplet splitting is somewhat overestimated by the results obtained by the above-mentioned analysis of the torque experiments which provides for the singlet-triplet splitting $E_1 = 22.0$ K,⁸ instead of 19.2 K obtained by fitting the specific-heat experimental data with a two level Schottky.

Similarly to what we have done for Fe_6 , in Fig. 2 we compare the specific-heat data of Fe_{10} with the curve obtained by Eq. (3) and the multiplet levels, and their anisotropy splitting, obtained by the torque experiments on this compound⁸ (see also the caption of Fig. 2 for further details). In this case also, Eq. (3) does not reproduce well the position of the 1.4 K maximum, and it turns out that the singlet-triplet splitting is overestimated by using the energy levels evaluated by the analysis of the torque experiments within the simplified spin-Hamiltonian approach [$E_1 = 6.4$ K (Ref. 8)].

It is interesting to note, generalizing the previous results, that the zero-field specific-heat data provide values of singlet-triplet splitting which are smaller than what obtained by other techniques. Taking the two-level Schottky fitting parameters $T_0 = 19.2$ and 4.56 K for Fe_6 and Fe_{10} , respectively, to characterize the specific-heat anomalies, it turns out that these values are indeed (slightly) smaller than those obtained from high-temperature susceptibility measurements in low fields [19.7 K for Fe_6 (Ref. 4) and 5.5 K Fe_{10} (Ref. 5), respectively]. More strikingly, the singlet-triplet splitting was found to be much higher (12 K for Fe_{10} and 38 K for Fe_6) when evaluated by NMR experiments.⁶ It is worth noting that magnetization and specific-heat experiments were carried out in the same range of temperature; thus one cannot

simply invoke a temperature change of the exchange coupling j to account for the low T_0 values obtained by specific heat. One may wonder whether this discrepancy arises from the special set of fitting parameters used in the analysis of the torque experiments, for which was assumed a conventional triplet splitting, characterized by an anisotropy term D_1 , in contrast to the oversimplified triply degenerated state of the two-level Schottky model. Yet, fitting the specific-heat data of Fe_{10} in the range $0.5 \text{ K} < T < 1.6 \text{ K}$ taking into account the triplet splitting, we obtain $E_1 = 4.79$ K (3.33 cm^{-1}) and $D_1 = 2.01$ K (1.40 cm^{-1}). These values are in agreement with the results of the two-level Schottky, yet E_1 is still much lower than what can be estimated from susceptibility measurements on powders.^{4,5} Thus, we are led to conclude that these discrepancies actually evidence some limitations of the simplified multiplets scheme and they ask for a more complex description of the cluster’s energy levels, beyond the strong exchange approximation.

We discuss in the following further characteristics of specific heat. In Fig. 2 one may compare the two-level Schottky curve with that obtained by Eq. (3), namely the many-level Schottky curve. We note that the two computed curves are quite different above the maximum, i.e., the two-level Schottky curve falls as T^{-2} , while the many-level model gives C/R values which hold close to 1 up to 20 K, due to the fact that multiplets with $S > 1$ give a non-negligible contribution above the maximum. Similar results were obtained for Fe_6 too, although they are not clearly visible in Fig. 3. The comparison with the experimental results on Fe_{10} shows that the contribution of multiplets with $S > 1$ cannot be neglected in order to reproduce the flat temperature dependence between 1.5 and 4 K (see Fig. 2). This is a feature of these molecular clusters and we learn that the use of T^{-2} fitting curve may lead to incorrect results in this class of compounds.

We analyze, hereafter, the lattice contribution to the specific heat of Fe_{10} . The lattice specific heat was evaluated by subtracting the magnetic contribution to the raw experimental data.¹⁴ In the temperature range 2–10 K, C_{latt} can be nicely fitted by a power law $C_{\text{latt}}/R = 0.0161T^{2.69}$ that is

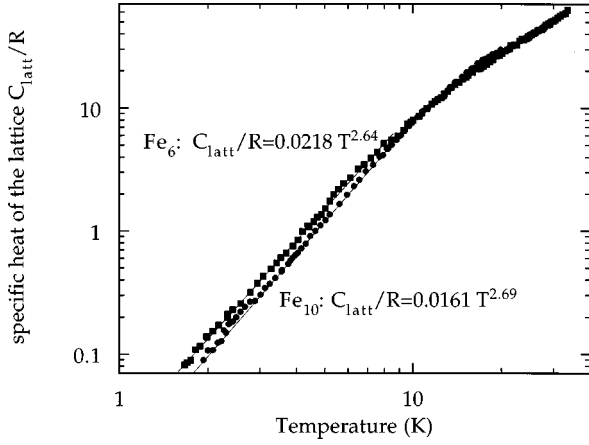


FIG. 4. Estimated lattice contribution C_{latt} to the molar specific heat for Fe₆ and Fe₁₀ compounds. At low temperature ($1.6 \text{ K} < T < 10 \text{ K}$) the temperature dependence of the lattice contribution can be approximated with a power law $\Delta C \sim T^\alpha$ with $\alpha = 2.64$ and 2.69 for Fe₆ and Fe₁₀, respectively.

quite similar to what we obtained for Fe₆. The lattice contribution, evaluated in such a way, is plotted in Fig. 4 with the analogous obtained for Fe₆: The two look very similar. This similarity can appear as a random coincidence, since these molecular compounds have different crystallographic structure, despite some generic similarities. However, preliminary results on other molecular magnets¹⁵ suggest that the observed power law T^α with $\alpha \sim 2.7$ fits the lattice contribution better than the commonly used T^3 law in this class of materials. Interestingly, similar power law T^α with $\alpha \sim 2.4$ – 2.8 was used to describe the lattice specific heat in (TMTSF)₂X ($X = \text{PF}_6$ and AsF_6) and (TMTTF)₂Br salts¹⁶ and ascribed to special low-dimensional phonon modes in those systems and similar behavior was also observed for one-dimensional conductor $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3.2(\text{D}_2\text{O})$.¹⁷ Alternatively, Gomes *et al.*¹² used a phenomenological combination of a linear and a cubic phonon term to describe the lattice contribution in Mn₁₂ and it is likely that the power law T^α simulates a polynomial expansion of a more complex curve whose origin should be better clarified.

We finally discuss the specific heat behavior observed at very low temperature on the Fe₁₀ compound, in particular the T^{-2} increase and the small bump at 0.2 K observed in the C vs T curve. We already noted that these anomalies show the presence of zero-field splitting within the molecular crystal with energies which are typical of nuclear hyperfine interactions. In order to see whether this can actually be the origin and which nucleus can give such a contribution to the specific heat, we make use of the simplified law:¹⁸

$$\frac{C}{R} = \frac{n}{3} \left(\frac{I+1}{I} \right) \left(\frac{\mu_n \mu_N H_{\text{eff}}}{k_B} \right)^2 \frac{1}{T^2},$$

where I and μ_n are, respectively, the spin and the magneton of the nucleus (the latter in units of nuclear magneton μ_N), n (i.e., the total number of atoms per molecule *times* the isotope fraction) is the number of active isotope per molecule and H_{eff} is the mean effective magnetic field acting on the nucleus (in Oe units). We can easily see that the ⁵⁷Fe isotope [$I = 1/2$, $\mu_n = 0.09$, isotope fraction = 2.1%, $n = 10 \times 0.021$

= 0.21, $H_{\text{eff}} = 330 \text{ KOe}$ (Ref. 18)] would give a negligible contribution, that is $C/R = 0.2 \times 10^{-4} T^{-2}$ instead of the measured $C/R = 5.5 \times 10^{-4} T^{-2}$. In the case of the two Cl species, ³⁵Cl ($I = 3/2$, $\mu_n = 0.82$, 75% of natural abundance) or ³⁷Cl ($I = 3/2$, $\mu_n = 0.68$, 25% of natural abundance), if all the 10 Cl nuclei are active one would obtain $H_{\text{eff}} \sim 350 \text{ KOe}$, which seems unphysically large considering their distant position from the Fe ions. More reasonable values can be obtained for protons. Taking, for instance, the case of protons ¹H ($I = 1/2$, $\mu_n = 2.79$) in the (OCH₃) group, we have $n = 60$ and this yields a value of $H_{\text{eff}} = 30 \text{ KOe}$ for the observed $C/R = 5.5 \times 10^{-4} T^{-2}$ behavior. With a much smaller fraction of active protons, say $n = 10$, we get $H_{\text{eff}} = 75 \text{ KOe}$. These H_{eff} values estimated for the protons in position of next neighbors are reasonable in the case of metals, yet for an insulator the H_{eff} is expected to decrease quite rapidly as one moves away from the magnetic ion. It should be also mentioned that NMR experiments on Fe₆ and Fe₁₀ compounds⁶ have shown that the magnetic field probed by protons, although in a different time scale with respect to our experiments, vanishes at the liquid-He temperature. Thus the origin of the effective magnetic field is not clear if one considers the ideal molecular crystal. On the other hand, it is certain that a small fraction of the Fe₁₀ sample contained defects⁵ and it is likely that some of these defects can give rise to zero-field splitting. This can actually be the origin, for instance, of the small bump with maximum at 0.2 K. However, if we compare the height of the observed $C/R = 5.5 \times 10^{-4} T^{-2}$ term with a calculated Schottky model we find that a non-negligible fraction of the sample ($>10\%$) must contribute to give such a $C/R = 5.5 \times 10^{-4} T^{-2}$ term. The reproducibility of the specific-heat values on the two samples studied and the quantitative agreement with the two-level Schottky model suggest, however, that the bulk of the sample was in good condition, therefore further experiments are needed to clarify whether the $C/R = 5.5 \times 10^{-4} T^{-2}$ contribution can simply be ascribed to defects or it is an intrinsic feature of the molecule.

CONCLUSIONS

Despite the huge lattice contribution, the main Schottky anomalies related to the singlet-triplet splitting of Fe₆ and Fe₁₀ magnetic rings have been observed in the low-temperature specific heat. We found that the Schottky maximum occurs at temperature lower than what one may estimate in the framework of simplified spin-Hamiltonian approach and on the basis of the magnetization experiments⁸ that we performed in parallel to this study. Since specific-heat measurements in zero field provide information in the limit of the vanishing Zeeman contribution, differently from most of the experimental techniques used so far to study these magnetic rings, we believe that this discrepancy arises from the fact that the Zeeman term, as well as the anisotropy, cannot be treated in a perturbative way. To corroborate this conjecture, it will be interesting to compare the zero-field splitting obtained by the specific heat with other measurements performed in the zero field such as the outstanding inelastic neutron-scattering experiments.

We observed some novel features of these systems, such as the flat C/R behavior above the Schottky maximum due to the non-negligible contribution of the excited states with $S > 1$ and the lattice contribution which follows a phenomenological power law $C/R \sim T^\alpha$ with $\alpha \sim 2.7$ for both compounds. Finally, two low-energy Schottky anomalies were also observed in Fe_{10} at very low temperatures $T \ll 1$ K, and ascribed to a small fraction of defected rings or to a hyperfine contribution.

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