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Low temperature specific heat of molecular rings: a study on the effects of the internal guest substitution and on the lattice contribution

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Abstract. The effects of the internal guest substitution within hexa-iron molecular rings (Na:Fe6 and Li:Fe6) have been investigated by means of low temperature specific heat (LTSH) measurements. By changing Na to Li as central metal ion, the Schottky anomaly shifts towards lower temperatures. The data analysis is supported by the study of the LTSH of the non-magnetic Na:Ga6 compound which has the same core structure as the iron rings. For the non-magnetic Na:Ga6, significant deviations from the simple $C \sim T^3$ Debye law were found and the use of conventional C *vs.* T fitting curves is critically discussed. The singlet-triplet energy gap ($E_1/k_\mathrm{B} = 12.1 \pm 0.5$ K) and its zero-field splitting ($D_1/k_\mathrm{B} = 1.5 \pm 1$ K) evaluated from the magnetic contribution of the Li:Fe6 LTSH are compared to values estimated by high field torque magnetometry.

PACS. 75.40.Cx Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.) – 75.50.-y Studies of specific magnetic materials

1 Introduction

The (supra-)molecular approach to the synthesis of large transition-metal clusters has recently provided a variety of new nanomagnetic materials [1]. Large magnetic clusters can now be synthesized in bulk quantities, so that their magnetic and thermodynamic properties can be studied in detail by conventional solid-state techniques. A great deal of work is nowadays devoted to magnetic clusters with high spin, such as the Mn_{12}-acetate [2] or Fe8 [3], that exhibit quantum tunneling of magnetization at low temperatures. Another class of molecular magnets made by almost coplanar metal (Fe, Cr) rings is also attracting increasing interest due to their high symmetry. Among them, rings made by even number (6, 10, 12, 18) of antiferromagnetically coupled Fe^{3+} ions have been found to have a non-magnetic ($S = 0$) ground state at low temperature [4,5]. Most of the low-temperature physical properties of such ferric wheels can be well described by including in the Hamiltonian nearest-neighbour (nn) Heisenberg interactions, magneto-crystalline (single ion) anisotropies, dipolar or anisotropic-exchange contributions and Zeeman interactions when an external magnetic field is applied. Different approaches [5,6] have been successfully used to solve such a hamiltonian and these have actually shown how the non-magnetic ground state is separated from the excited magnetic multiplets by gaps regularly spaced in energy. One of the most intriguing challenge is however the control of the magnetic characteristics of these clusters by means of structural and chemical changes. The cyclic hexa-iron clusters have shown strong tendency to trap alkali-metal ions that, in turns, control the topology of the oxygen bridges between Fe ions. This suggested the possibility of tuning the magnetic properties of these materials by simply changing the internal guest [7]. This work, carried out in parallel to studies of magnetic anisotropy by a torque magnetometer in high magnetic field [8,9], is actually devoted to the study of the effects of the Na substitution by Li in the hexa-iron molecular rings.

Since the energy gap between the lowest-lying levels is typically of the order of a few (5-20) K, the study of specific heat seems to be particularly suitable for measuring the energy gap between the lowest-lying levels. Schottky anomalies, with unique shape, are indeed observed at few K [10]. Moreover, low temperature specific heat (LTSH) measurements do not need the application of an external magnetic field. From this point of view, LTSH measurements are complementary to other techniques used so far to study the molecular magnets. These metal clusters

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are, however, embedded in a molecular matrix that typically contains a few hundreds of atoms. This implies that the lattice contribution to the specific heat (C) is huge even at low temperature, obscuring, in general, the Schottky anomaly (this issue is encountered each time one tries to apply solid state techniques to molecular materials or, more in general, to nano-particles embedded in amorphous or organic matrix). Moreover, significant deviations from the conventional Debye $C \sim T^3$ law have been already observed for molecular magnets [10,11], so that a detailed investigation of the lattice term seems now mandatory. These facts motivated the study of the temperature dependence of the specific heat of the non-magnetic Na:Ga6 rings, recently synthesised in our laboratory. On the basis of extended Debye's and Einstein's models, we propose C *vs.* T fitting expressions that we will use to evaluate the lattice contribution of magnetic Li:Fe6.

2 Experimental techniques and sample features

Low temperature heat capacity measurements were performed by means of a continuously refilled ^{4}He evaporation cryostat and by using the quasi-adiabatic method. Polycrystalline samples were pressed, without any additive (glue or Cu powder), in pellets of 8 mm diameter and with typical mass of ~100 mg. The specimen was clamped, with the help of a small quantity of Apiezon N grease, between two Si plates on which thermometer (Lake Shore Cernox) and heater were attached and mounted on different sides of the sample. The intensity of the heat pulse was chosen to obtain a temperature variation $\Delta T \leq 2\%$ of the bath temperature.

Microcrystalline powders have been prepared by the procedure described elsewhere [7]. The molecular crystals studied in this work have chemical formula:

$$[\mathrm{LiFe_6(OCH_3)_{12}(C_{15}H_{11}O_2)_6}]\mathrm{PF_6} \qquad \text{(Li:Fe6)}$$
$$[\mathrm{NaGa_6(OCH_3)_{12}(C_{17}H_{15}O_4)_6}]\mathrm{ClO_4} \qquad \text{(Na:Ga6)}$$

and they are often compared to:

$$[\mathrm{NaFe_6(OCH_3)_{12}(C_{17}H_{15}O_4)_6}]\mathrm{ClO_4} \qquad \text{(Na:Fe6)}$$

whose LTSH was studied in a previous work [10]. Li:Fe6, Na:Fe6 and Na:Ga6 crystallize in a trigonal $\mathrm{R}\bar{3}$ space group and they have similar core structure which comprises six-membered rings of Fe^{3+} or Ga^{3+} ions in a coplanar configuration (see Fig. 1). The methoxide ligands ($\mathrm{OCH_3}$) bridge neighbouring metal ions and support the cyclic skeleton. The guest alkali-metal ion (either Li or Na) is placed in the centre of the metal crown and it contributes to tune both the nearest neighbour Fe-Fe distance (3.2152 Å and 3.140 Å for Na:Fe6 and Li:Fe6 respectively) and the geometry of the bridging oxygen ligands [7]. Each metal ion is further coordinated by chelating β-diketonate ligand, either the dbm ($\mathrm{C_{15}H_{11}O_2}$) or pmdbm ($\mathrm{C_{17}H_{15}O_4}$). The crystal lattice also contains variable amounts of disordered solvent molecules ($\mathrm{CHCl_3}$ and $\mathrm{CH_3OH}$) which are partially or totally removed during the drying procedure. The number of the atoms per cluster, estimated by chemical analysis, is ca. 242, 288, and 313 for Li:Fe6, Na:Fe6 and Na:Ga6, respectively.

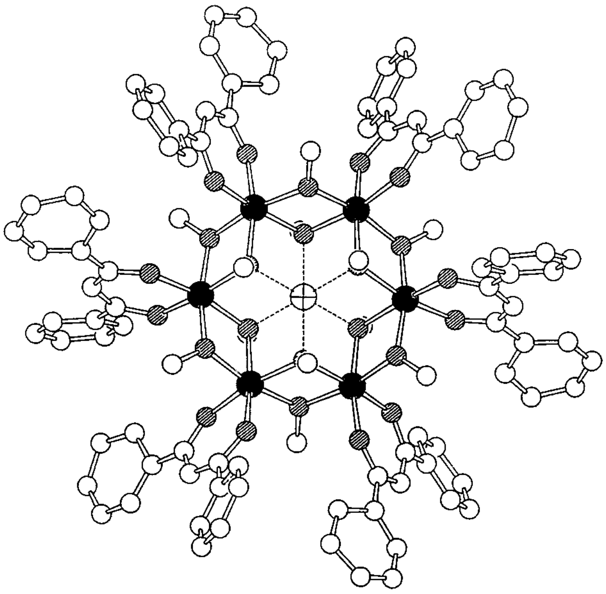


Fig. 1. Molecular structure of Li:Fe6. Black full circles: Fe ions; circle with cross at the centre of the crown: Li ion; dashed circles: oxygen ions; empty circles: carbon ions. Hydrogen atoms have been omitted for clarity.

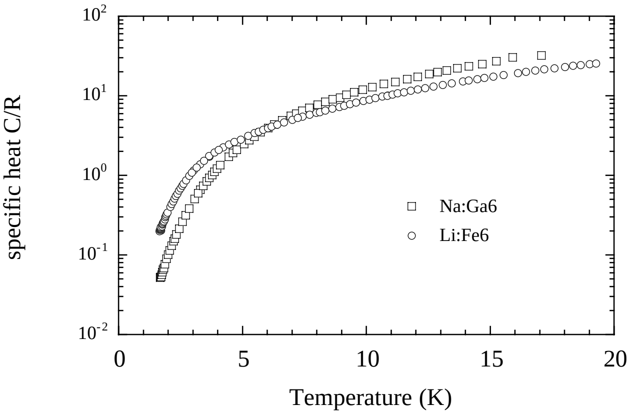


Fig. 2. Temperature dependence of specific heat (C normalized to the gas constant R = 8.314 J/moleK) of magnetic Li:Fe6 and non-magnetic Na:Ga6.

3 Results

In Figure 2 the specific heat (C) of Li:Fe6 normalized to the gas constant R = 8.314 J/moleK can be compared with that of the non-magnetic Na:Ga6. It can be noticed that between 10 K and 20 K the specific heats of these molecular rings look similar, although the C/R values of Na:Ga6 is slightly higher than that of Li:Fe6. In this temperature range the lattice contribution dominates and it

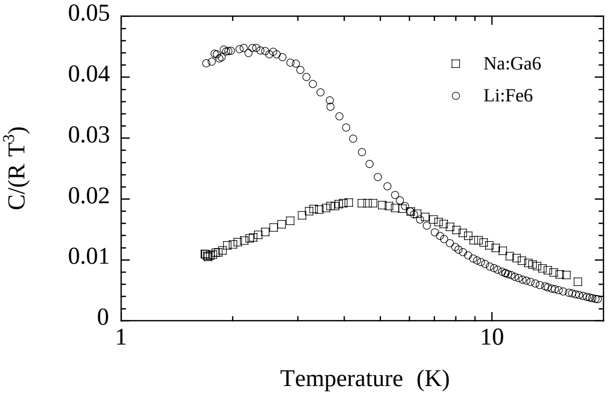


Fig. 3. Temperature dependence of $C/(RT^3)$ for magnetic Li:Fe6 and non-magnetic Na:Ga6.

is not surprising to find this similarity. Differences are evident below ∼10 K where the specific heat of Na:Ga6 falls much faster than the C/R of the iron-based compound. This evidences the presence of an additional magnetic contribution at the lowest temperatures in the LTSH of Li:Fe6. A comparison between the different behaviour of these compounds can be also observed in the $C/(RT^3)$ *vs.* T plot of Figure 3. In the magnetic Li:Fe6 compound, the Schottky anomaly is evidenced by the maximum of the $C/(RT^3)$ *vs.* T curve (hump) at ∼2.2 K. A broader anomaly of the $C/(RT^3)$ *vs.* T curve is also present in the data of Na:Ga6 and it should be ascribed to the lattice since there is no magnetic ion in this compound. Moreover, the $C/(RT^3)$ data of Na:Ga6 – as well as those of Li:Fe6 – have non-monotonic temperature dependence above 10 K indicating that corrections to simplified Debye T^3 law have to be considered.

4 Analysis of the specific heat data of Na:Ga6

The huge number of ions per molecule (a few hundreds) and the lack of additional information on the lattice dynamics do not allow to develop a detailed and rigorous model for the lattice contribution of the LTSH. However we present here an analysis of the LTSH data of non-magnetic Na:Ga6 based on conventional models [12]. Although structural differences exist among these molecular rings, we propose to consider the specific heat of Na:Ga6 as a model for the lattice contribution C_{latt} to the LTSH of this class of molecular compounds.

We first assume that samples are in a perfectly crystalline form [13] thus we consider two contributions to the lattice specific heat: a Debye's term C_{D} and an Einstein's term C_{E} that account for the acoustic and the optic-like modes respectively:

$$C_{\text{latt}} = C_{\text{E}} + C_{\text{D}}$$

with:

$$\frac{C_{\text{E}}}{R} = 3r_{\text{E}}\left(\frac{T_{\text{E}}}{T}\right)^2 \frac{\exp\left(\frac{T_{\text{E}}}{T}\right)}{\left[\exp\left(\frac{T_{\text{E}}}{T}\right) - 1\right]^2}$$

r_{E} is the number of free Einstein-like modes in one molecule and, since the fraction of such oscillators are not known, it is left as a free fitting parameter. In the cases in which non-linear dispersion relation has to be taken into account, the Debye's term C_{D} may assume two different – but equivalent – polynomial forms [14] *i.e.*:

$$1)\ \frac{C_{\text{D}}}{R} = aT^3 + bT^5 + cT^7$$

$$2)\ \frac{C_{\text{D}}}{R} = \frac{234 r_{\text{D}} T^3}{\left[\theta_{\text{D}} + \varepsilon T^2 + \delta T^4\right]^3}\,.$$

Within the framework of the Debye's model and in the limit of vanishing temperature, $r_{\text{D}} = 1$ and only the lowest order T^3 should remain in the polynomial laws thus the a coefficient can be written as:

$$a = \frac{12}{5}\frac{\pi^4}{\theta_{\text{D}}^3} \sim \frac{234}{\theta_{\text{D}}^3}, \quad a \text{ in K}^{-3} \text{ units},$$

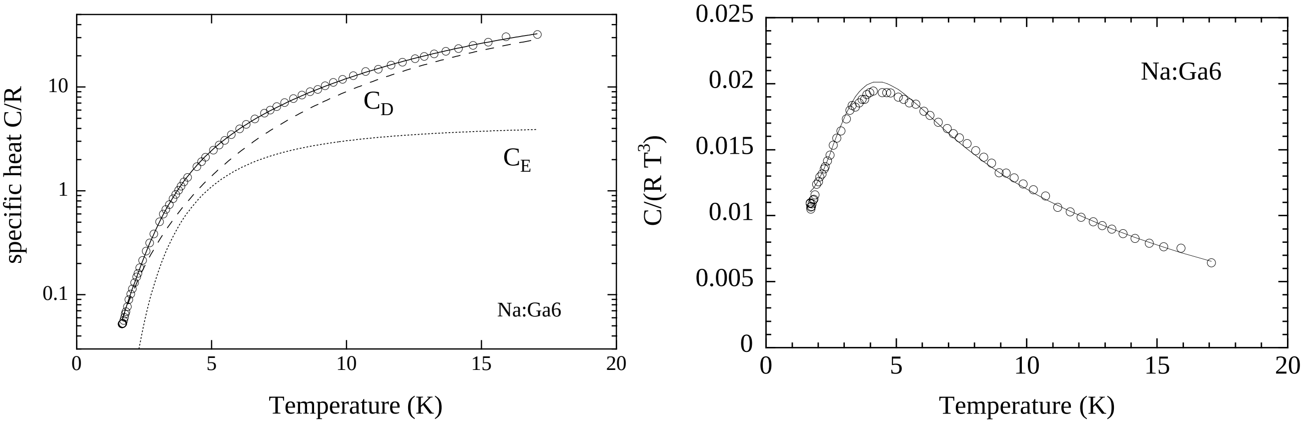
with θ_{D} defined in a strictly acoustic sense. Specific heat data of Na:Ga6 between 1.6 K and 17 K can be well fitted by using the parameters reported in Table 1.

The quality of the fitting procedure is equivalent (same χ^2) for expressions (1, 2), although it should be noted that the presence of the δT^4 term in (2) does not seem to significantly improve χ^2. Therefore it is also possible to simplify curve (2) by omitting this term for the temperature range analysed here. In Figure 4a the C/R *vs.* T of Na:Ga6 is plotted with the best fit (curve (2)). We also plot both the estimated Einstein's and Debye's contributions in order to show the weigh of each term in the different temperature range. In Figure 4b the specific heat data and the fitting curve are plotted in a $C/(RT^3)$ *vs.* T^2 form. It is clear from this plot that the Einstein's contribution C_{E} is necessary to account for the hump at $T \sim 4.5$ K while, at the highest temperatures, $C/(RT^3)$ slightly decreases indicating that the increase of C/R is slower than T^3. This feature can be also seen in the results of the fitting procedure: The polynomial law (1) contains a T^5 term with a negative coefficient and in curve (2) the ε coefficient of T^2 is positive. These are anomalies for a Debye lattice contribution since in simpler materials the sign of these coefficients is reversed [14].

The fitting curve (2) allows a somewhat deeper interpretation of the results. θ_{D} represents the Debye temperature in the limit of the low temperature. We found $\theta_{\text{D}} \sim 27$ K which is a very low value, quite close to the temperature range in which the C/R *vs.* T curve is studied. It is clear that, within the framework of the Debye model, we deal with an intermediate temperature regime ($T \leq \theta_{\text{D}}$) whereas a purely T^3 regime should be obeyed only for $T < \theta_{\text{D}}/50$. In this case, it can be more convenient to put r_{D} close to the number of ions in the molecule (313, in the case of Na:Ga6) fixing, in this way, C_{D} close to the Dulong-Petit value, *i.e.* the limit of C_{latt} at high temperature. Fixing $r_{\text{D}} = 313$ (and $r_{\text{E}} = 1.50$, $T_{\text{E}} = 22.2$ K), we obtain $\theta_{\text{D}} = 184$ K and $\varepsilon = 0.169$ (see Tab. 1). This θ_{D} value can be regarded as an average over all the phonon modes active below 20 K and it seems to be more realistic.

Table 1. Parameters obtained by the best fit of the Na:Ga6 LTSH data with expressions (1, 2) reported in the text. The relative chi-square χ^2 parameter is evaluated taking all data between 1.6 and 17 K with the same statistical weight.

Debye's term C_D/R	Einstein's term C_E/R	χ^2
$a = 0.01149$; $b = -2.719 \times 10^{-5}$; $c = 2.6115 \times 10^{-8}$	$r_\mathrm{E} = 1.46$; $T_\mathrm{E} = 21.59$(K)	2.97
$\theta_\mathrm{D} = 26.9$ K; $\varepsilon = 0.027$; $\delta = -5.6 \times 10^{-6}$; $r_\mathrm{D} = 1$	$r_\mathrm{E} = 1.50$; $T_\mathrm{E} = 22.2$(K)	2.76
$\theta_\mathrm{D} = 184$ K; $\varepsilon = 0.169$; $\delta = 0$; $r_\mathrm{D} = 313$	$r_\mathrm{E} = 1.50$; $T_\mathrm{E} = 22.0$(K)	2.80



(a)

(b)

Fig. 4. (a) Best fit of the low temperature specific heat of Na:Ga6 with the $C_\mathrm{E} + C_\mathrm{D}$ (curve 2) reported in the text. Fitting parameters are reported in Table 1. (b) Comparison of experimental data with the best fit in a $C/(RT^3)$ *vs.* T plot.

For what concerns the Einstein-like contribution, we note that r_E is of the order of the unity indicating that very few low-frequency oscillators are active at low temperature. The Einstein-like contribution C_E may account for optical phonon branches as well as for branches with flat dispersion. It should be noted however that T_E is unusually low for a crystal and it is likely that the hump in the C/T^3 *vs.* T can be due to localized oscillators rather than collective modes. Moreover it is worth to remind that a hump in the $C/(RT^3)$ *vs.* T similar to what reported in Figure 4b is also observed in amorphous materials [15,16]. Generally in these cases data can not be well fitted by an Einstein's curve since the hump is broader in amorphous than in crystalline materials. However, since there can be small amount of amorphous solvent in the sample, we can not rule out this origin of the hump.

We finally note that if we restrict our attention to data below 10 K, a sufficiently good quality of fitting procedure can be also obtained with a small number of free parameters. The simplest way is to use a phenomenological power law for the acoustic contribution. For Na:Ga6 we found that $C_\mathrm{D}/R = 0.0157T^{2.64}$, in addition to C_E, fits well data below 10 K. Note that a very similar power law fits quite well LTSH data of Na:Fe6 ($C_\mathrm{D}/R = 0.0218T^{2.64}$) and Fe10 ($C_\mathrm{D}/R = 0.0161T^{2.69}$) [10] and this supports the validity of this simple phenomenological law in a short temperature range.

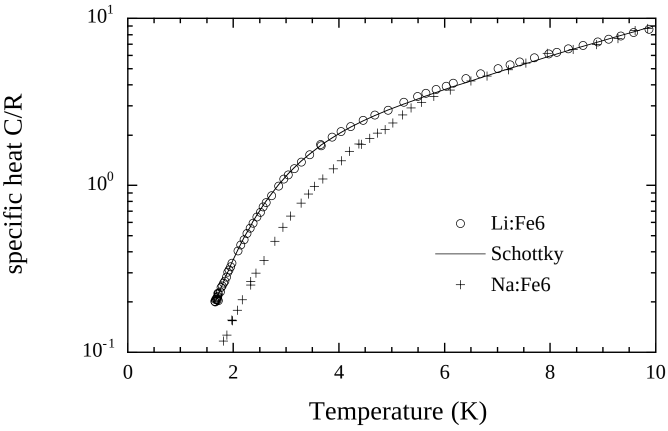


Fig. 5. Comparison between the specific heat of Na:Fe6 (from Ref. [10]) and that of Li:Fe6. The continuos line is the best fit of the Li:Fe6 data with a simple Schottky law plus a power law that accounts for the lattice contribution.

5 Analysis of the Li:Fe6 specific heat data

The LTSH of Li:Fe6 can be compared with data of Na:Fe6 in Figure 5. The C/R values overlap each other at $T \geq 8$ K, where the lattice contribution C_latt dominates, while below ∼6 K the drop of the Li:Fe6 specific heat, which mostly includes the magnetic contribution C_m, is clearly shifted towards lower temperatures as compared to that of Na:Fe6. This evidences, without the help of any quantitative analysis, the effects of the internal guest substitution (Na by Li) on the energy levels of the iron rings. The presence of the smallest Li guest slightly reduces the Fe-Fe distance and, most importantly, displaces the oxygen bridges between metal Fe ions [7]. It turns out that the antiferromagnetic exchange coupling reduces by substituting Na by Li and the magnetic anisotropy changes too as a consequence of the more regular topology of the oxygen atoms in Li:Fe6 as compared to the arrangement in Na:Fe6 [7].

A simple quantitative analysis of LTSH can be performed by fitting the C/R *vs.* T curve of Li:Fe6 with a Schottky law [12]:

$$\frac{C_\mathrm{S}}{R} = \frac{g_0}{g_1}\left(\frac{T_0}{T}\right)^2 \frac{\exp\left(\frac{T_0}{T}\right)}{\left[1+\frac{g_0}{g_1}\exp\left(\frac{T_0}{T}\right)\right]^2}$$

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 take $g_0 = 1$ (ground state = singlet) and $g_1 = 3$ (first excited state = triplet). The continuous line in Figure 5 is the best fit of the Li:Fe6 data below 6 K obtained with $T_0 = 14.5 \pm 0.5$ K and a lattice contribution $C_\mathrm{latt} = 0.0538\ T^{2.2}$. For Na:Fe6 we found $T_0 = 19.2$ K [10] *i.e.* a larger energy gap between the lowest-lying levels.

With the simple model used above, the error in the determination of T_0 is mainly due to the rough evaluation of the lattice contribution C_latt moreover we have no information on the zero field splitting of the lowest-lying levels. We proposed in the following a more sophisticated analysis of the Li:Fe6 data.

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

$$\frac{C_\mathrm{m}}{R} = \beta^2 \times \frac{\sum_i E_i^2 \exp(-\beta E_i) \sum_i \exp(-\beta E_i) - \left[\sum_i E_i \exp(-\beta E_i)\right]^2}{\left[\sum_i \exp(-\beta E_i)\right]^2}.$$

where $\beta = (k_\mathrm{B}T)^{-1}$. For Li:Fe6 we assume that the hexairon rings keep the axial symmetry and that the Heisenberg interactions is the dominant one. The pattern of low-lying energy levels can be consequently sketched as follows:

$$E_i = E_S + D_S(M_S^2 - S(S+1)/3)$$

where $S = 0, 1, 2$, etc. is the total-spin quantum number and $M_S = 0, \pm 1, ... \pm S$. E_S and D_S are respectively the energy gap and the axial zero-field splitting parameters of the different multiplets. We choose E_1 and D_1 as free parameters, keeping fixed E_2 and D_2 to the values obtained by torque magnetometery experiments ($E_2/k_\mathrm{B} = 41.46$ K and $D_2/k_\mathrm{B} = 0.425$ K respectively [8]) and neglecting contributions of higher excited states. Taking a simple polynomial law for the lattice contribution and omitting the Einstein's contribution we obtain

$$E_1 = 14.2 \pm 0.5 \text{ K} \quad \text{and} \quad D_1 = 3.8 \pm 1 \text{ K}.$$

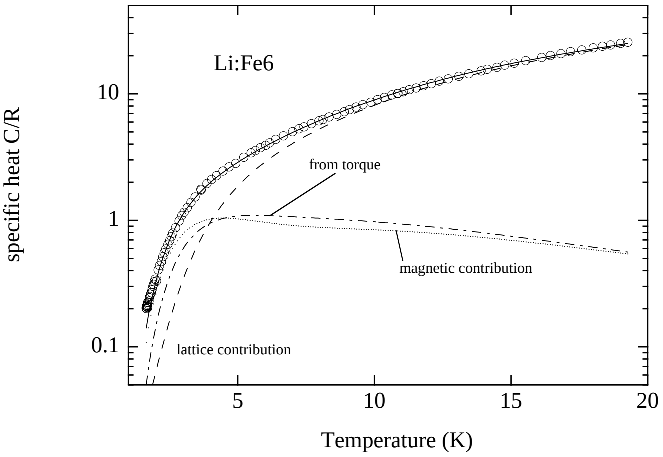


Fig. 6. Best fit of the specific heat of Li:Fe6 with the $C_\mathrm{m}+C_\mathrm{latt}$ law presented in the text. The estimated magnetic and the lattice contributions are separately plotted for comparison as well as the magnetic contribution estimated from the parameters obtained by high field torque magnetometry experiments.

Further improvement can be achieved by considering a more realistic lattice contribution. We previously showed that a combination of conventional Debye's and Einstein's laws may well account for the lattice contribution of the LTSH of non magnetic Na:Ga6 and we assume that this holds for Li:Fe6 (and Na:Fe6) too, although these crystals are not wholly isomorphic. We also found that the main Debye's parameters should be regarded as an average over several oscillators rather than an intrinsic features of the acoustic branches while the Einstein's contribution accounts for specific – probably localized – oscillators. Since Na:Ga6 contains more atoms (313) than Li:Fe6 (242) and Na:Fe6 (288), it is not surprising to found that the C/R of Na:Ga6 rises more rapidly above 10 K (see Fig. 2) since it should saturate to higher value at high temperature (the Dulong-Petit law) as compared to the specific heat of the iron-based compounds. We fixed $r_\mathrm{D} = 242$ for Li:Fe6 (and $r_\mathrm{D} = 288$ for Na:Fe6) and we determine the θ_D, ε, r_E and T_E parameters by fitting data above ∼8 K firstly. In this temperature range the lattice contribution is much higher than the magnetic one and we may safely take a preliminary estimation of C_m by using, for instance, the energy levels obtained by torque magnetometery [8]. Once the lattice parameters have been determined, C_m can be estimated by fitting data below ∼8 K. This procedure can be iterated and it converges after few times. Results for Li:Fe6 and Na:Fe6 are summarized in Table 2.

As preliminary check, we first note that by applying this procedure to Na:Fe6 data we obtain E_1/k_B and D_1/k_B values quite close to those we got by a simpler analysis [10]. In Figure 6 the best fit is compared with C/R data of Li:Fe6. In this figure we also plot both the lattice and the magnetic contributions. It can be noticed, as we already anticipated, that the lattice specific heat actually

Table 2. Lattice and magnetic parameters obtained by the best fit of the LTSH data as described in the text. The Debye's contribution is curve (2) mentioned in the analysis of Na:Ga6 data.

	Debye's term C_{D}/R	Einstein's term C_{E}/R	E_1/k_{B} (K)	D_1/k_{B} (K)
Li:Fe6	$\theta_{\mathrm{D}} = 217.8$ K; $\varepsilon = 0.142$; $r_{\mathrm{D}} = 242$	$r_{\mathrm{E}} = 1.70$; $T_{\mathrm{E}} = 21.97$ K	12.1 ± 0.5	1.5 ± 1
Na:Fe6	$\theta_{\mathrm{D}} = 209.8$ K; $\varepsilon = 0.172$; $r_{\mathrm{D}} = 288$	$r_{\mathrm{E}} = 1.05$; $T_{\mathrm{E}} = 21.59$ K	20.2 ± 1	8.6 ± 1.5
Na:Ga6	$\theta_{\mathrm{D}} = 184$ K; $\varepsilon = 0.169$; $r_{\mathrm{D}} = 313$	$r_{\mathrm{E}} = 1.50$; $T_{\mathrm{E}} = 22.0$ K		

dominates above ~10 K, while C_{m} and C_{latt} are of the same order of magnitude at the liquid helium temperature. This is a typical feature of these antiferromagnetically coupled iron rings [10].

It is worth to briefly discuss the accuracy of the previous results. The error reported for E_1 and D_1 are estimated by considering the mutual dependence of these parameters. In other words, by slightly changing the energy gap E_1 (or alternatively D_1) it is possible to obtain a fit of comparable quality (same χ^2) with an anisotropy parameter D_1 (or E_1) determined within the error reported in Table 2. A different source of error arises from the evaluation of the lattice contribution. The different data analysis reported above give an idea on how much the E_1 and D_1 values depend on the choice of the C_{latt} *vs.* T expression. Note that the presence of the Einstein's term, suggested by the analysis of the Na:Ga6 data, slightly changes the E_1 and the D_1 parameters.

Finally it is worth to compare the results of Table 2 with those obtained by measurements of magnetic anisotropy ($E_1/k_{\mathrm{B}} = 13.9$ K and $D_1/k_{\mathrm{B}} = 1.4$ K) on Li:Fe6 single crystals [8]. For a visual comparison, we plot in Figure 6 the magnetic contribution to C/R estimated by using the parameters obtained by the above mentioned magnetic measurements. The agreement with the specific heat analysis is quite good, yet we may notice that the E_1 value evaluated by the specific heat experiments is slightly smaller (14%) than that obtained by measurements in high magnetic field. Although this difference is within the accuracy of the analysis of the LTSH data, it is worth to remind that also for Fe10 rings the Schottky anomaly appears at temperatures lower than what one may expect from the results obtained by measurements of magnetic anisotropy. The outstanding neutron scattering experiments on Li:Fe6 will better clarify the origin of this discrepancy.

In conclusion, we used LTSH experiments to show the effects of internal guest substitution on the lowest-lying energy levels of magnetic hexa-iron clusters. We have also reported the study of the LTSH of the non-magnetic Na:Ga6 molecular clusters and we believe that our analysis can be successfully used to estimate the lattice contribution of other molecular magnets. By comparing results of different analysis, we have also estimated the accuracy with which the energy gap and the zero field splitting can be determined in these class of materials by specific heat measurements. Finally, we found that the singlet-triplet energy gap estimated here by LTSH measurements is slightly weaker than what obtained by high field torque magnetometry data [8], confirming what we already noted for the Fe10 ferric wheels [10]. This issue still needs to be clarified.

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