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Low-lying magnetic excitations and magnetocaloric effect of molecular magnet $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$

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Abstract – Low-temperature heat capacity measurements were performed on the molecular nanomagnet $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ (V15). The low-lying magnetic excitations are clearly evidenced by the Schottky anomalies in the specific-heat data. The energy levels determined from the low-temperature observables agree well with the three-spin model for V15. The magnetocaloric effect of V15 is examined. The maximum entropy change of $5.31\,\text{Jkg}^{-1}\text{K}^{-1}$ is found for a field change of $\Delta H = (8-0.5)\,\text{T}$ at $\sim$1.5 K. In spite of the low ground-state spin of V15, a drastic entropy change of $4.12\,\text{Jkg}^{-1}\text{K}^{-1}$ is observed for a field change of $\Delta H = (8-0.05)\,\text{T}$ at 0.4 K, which is comparable to the entropy change of some high-spin sub-kelvin magnetic coolers at such low temperatures. Anisotropy and consequent zero-field splitting result in this characteristic of V15 and may open new possibilities in the design of ultra-low-temperature molecular coolers.

Introduction. – Molecular magnets provide ideal testbeds for important scientific concepts in mesoscopic physics and have potential applications in magnetic storage, magnetoeletronics, magnetic refrigeration, and quantum computing [1]. This class of magnets are composed of identical magnetic molecules, which interact via negligibly small dipole-dipole interactions. Each molecule contains a small cluster of magnetic ions with strong magnetic interactions and thus possesses a total magnetic moment. The magnetic properties of the individual magnetic molecule are accessible by means of macroscopic characterization methods.

The magneto-caloric effect (MCE) is the change of magnetic entropy and the related adiabatic temperature following a change of the applied magnetic field. The technique of adiabatic demagnetization based on the MCE is of great technological importance because it is energy-efficient and provides an alternative to conventional ^{3}He-^{4}He dilution refrigerator for cooling applications in the ultra-low-temperature region [2,3]. In conventional refrigerant materials, such as paramagnetic salts, the residual interactions between magnetic dipoles often lead to a spin ordering or a spin-glass transition at low temperatures, limiting the lowest temperature that can be reached. Geometrically frustrated magnets are suggested as prospective candidates for use in adiabatic demagnetization at low temperatures, since the strongly frustrated spins remain in a disordered cooperative paramagnetic state even well below the Curie-Weiss temperature [4,5]. Recently, molecule-based magnets have also attracted interest in the area of magnetic refrigeration, mainly due to the high spin value and the vanishing magnetic anisotropy that can be realized in such systems [6]. In combination of spin frustration and certain high-symmetry zero-dimensional molecular structure, frustration-enhanced MCE could be possible [7].

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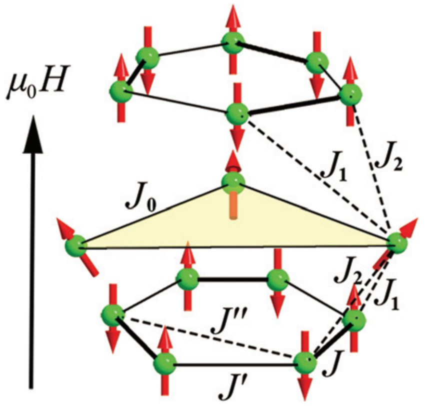

Fig. 1: (Colour on-line) Schematic view of the spin cluster V15 with $\mu_0 \boldsymbol{H}$ being the external magnetic field. Exchange couplings between the spins are shown and reported in the text. The central spin triangle is highlighted.

The low-spin weakly anisotropic molecular magnet, $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ (V15), has been attracting considerable attention due to its importance for both fundamental science and the implementation of quantum computation [8,9]. As illustrated in fig. 1, each V15 cluster consists of 15 V^{4+} (spin-(1/2)) ions, whose structure can be divided into three layers with different magnetization: a large central triangle and two hexagons sandwiching the central triangle. Each hexagon consists of three pairs of strongly coupled spins with the antiferromagnetic (AF) exchange parameter $J \approx 800\,\mathrm{K}$. Other AF exchange interactions inside the hexagons are $J' \approx 150\,\mathrm{K}$ and $J'' \approx 300\,\mathrm{K}$ [10–13]. The magnetization of hexagons is quenched at low temperatures due to the strong AF couplings. The spins in the central triangle are coupled antiferromagnetically to the spins on hexagons via J_1 and J_2, which cancel each other to a large extent ($J_1, J_2 \ll J$) [10–14]. The spins in the central triangle are weakly coupled with AF exchange parameter $J_0 \approx 2.5\,\mathrm{K}$, governing the magnetic properties of V15 at low temperatures ($T < 20\,\mathrm{K}$) [8]. In order to understand the low-temperature (low-T) magnetism of V15, an approximate three-spin model was proposed and substantiated on the basis of the exact diagonalization of the spin Hamiltonian of V15 [13,15,16]. In this model, the 15 spins can be divided into three groups. Each group consists of one spin from the central triangle and its four nearest neighbors in the outer hexagons. Each group possesses a total spin of 1/2 and the V15 cluster can be presented as three effective $S_i = 1/2$ spins occupying the corners of the central triangle.

Considering a Heisenberg antiferromagnetic model on a spin triangle, the low-T magnetic levels of V15 under the external magnetic field $\mu_0 \boldsymbol{H}$ can be simply expressed by the spin Hamiltonian

$$H_0 = (J_{12}\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + J_{23}\boldsymbol{S}_2 \cdot \boldsymbol{S}_3 + J_{31}\boldsymbol{S}_3 \cdot \boldsymbol{S}_1) + g\mu_B \mu_0 \boldsymbol{H}\left(\boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3\right), \qquad (1)$$

where $\boldsymbol{S}_1$, $\boldsymbol{S}_2$, $\boldsymbol{S}_3$ denote the effective spin operators, and J_{ij} is the Heisenberg exchange parameter between the effective spins i and j. Taking the equilateral triangle case ($J_{ij} = J_0 > 0$) as a first approximation, the ground state consists of two degenerate $S = 1/2$ Kramer's doublets and it is separated from the $S = 3/2$ quartet excited state by $3J_0/2 \approx 3.8\,\mathrm{K}$. This part of energy spectrum is well separated from other higher energy levels [8]. Hereunder the spin functions will be labeled as $|S_1 S_2 (S_{12}) S_3 S M\rangle \equiv |(S_{12}) S M\rangle$ with S_{12} being the intermediate spin ($\boldsymbol{S}_{12} = \boldsymbol{S}_1 + \boldsymbol{S}_2$).

In this paper, we determine the low-lying excitations through characteristic Schottky anomalies by measuring the heat capacity of a V15 single crystal down to 70 mK. The heat capacity result reveals a rich picture for the low-lying magnetic energy spectrum of V15 and clearly depicts the field dependence of these energy levels. The ultra-low-T MCE of V15 will be evaluated and discussed in this paper.

Experimental details. – The black V15 single crystals were synthesized following the procedures as described in [9]. A small crystal with a mass of 1.3 mg was used in the heat capacity measurements. The measurements were performed on a Quantum Design physical property measurement system equipped with a liquid-helium cryostat and a dilution insert device. The heat capacity at constant pressure was measured with thermal relaxation technique under a two-tau model [17]. The heat capacity of the sample was determined via two separate measurements. First, the heat capacity of the addenda, including the sample platform, the thermometer, the heater, and the Apiezon N grease, was measured. Second, the total heat capacity of the sample and the addenda was measured. Then the heat capacity of the sample was determined by subtracting the heat capacity of the addenda from the total heat capacity.

Results and discussion. – The molar specific heat of V15 was first measured from 70 mK to 260 K in zero external magnetic field (data above 6 K not shown). There is no magnetic phase transition within the investigated temperature range, as expected in V15 as a spin-frustrated molecular magnet. Lacking a non-magnetic reference, the lattice contribution to the specific heat of V15 cannot be determined without any model. The fit with the Debye model using a single Debye temperature cannot reproduce the lattice specific heat within the temperature range of 70 mK–260 K. The following discussion will focus on the low-T ($T < 6\,\mathrm{K}$) region, where the Schottky anomalies dominate so that the lattice specific heat can be safely approximated to exhibit a cubic dependence on temperature.

Figure 2 illustrates the specific heat of V15 measured from ∼70 mK to 6 K in various external fields ranging from 0 to 8 tesla. The direction of the external field at the sample position was parallel to the c-axis of the crystal. Below 0.5 T, we can clearly see two humps at ∼0.1 and ∼1.5 K, which are Schottky anomalies originating from

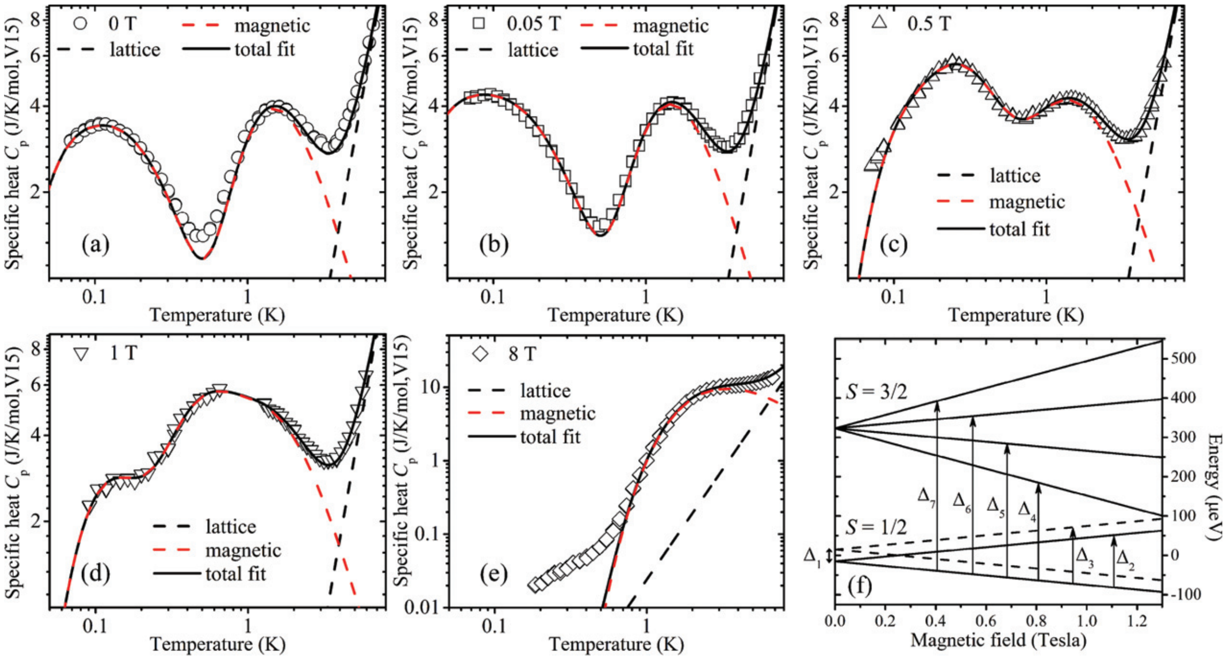

Fig. 2: (Colour on-line) Temperature dependence of the specific heat of V15 in a field of 0 (a), 0.05 (b), 0.5 (c), 1 (d), and 8 (e) tesla, together with the lattice (black dashed lines), magnetic (red dashed lines), and total (black solid lines) fits; (f) low-lying energy spectrum of V15 within the three-spin model. The definitions of the energy gaps $\Delta_{1\text{–}7}$ are illustrated as arrows.

the low-lying magnetic excitations [18]. Hereunder the two Schottky anomalies at ~0.1 and ~1.5 K are denoted as Schottky 1 and Schottky 2, respectively. They change with the external field, indicative of their magnetic origin. The lattice contribution to the total specific heat within this temperature range can be approximated to be one Debye term with cubic dependence on temperature,

$$C_{\mathrm{Debye}} = 234 \cdot R \cdot r_{\mathrm{D}} \cdot T^3/\Theta_{\mathrm{D}}^3, \tag{2}$$

where R is the gas constant, Θ_{D} is the Debye temperature, $r_{\mathrm{D}} = 96$ is the number of atoms per V15 molecule. The two Schottky anomalies are fitted with the Schottky model for a multi-level system, which is expressed by

$$\begin{aligned} C_{\mathrm{Sch}} = {} & \frac{R}{k_{\mathrm{B}}^2 T^2} \frac{\sum\limits_i \varepsilon_i^2 \exp\left(-(\varepsilon_i/(k_{\mathrm{B}}T))\right)}{\sum\limits_i \exp\left(-(\varepsilon_i/(k_{\mathrm{B}}T))\right)} \\ & - \frac{R}{k_{\mathrm{B}}^2 T^2} \frac{\left[\sum\limits_i \varepsilon_i \exp\left(-(\varepsilon_i/(k_{\mathrm{B}}T))\right)\right]^2}{\left[\sum\limits_i \exp\left(-(\varepsilon_i/(k_{\mathrm{B}}T))\right)\right]^2}, \end{aligned} \tag{3}$$

where ε_i is the energy of spin level i. The Schottky anomaly arises from the entropy change caused by the thermal population of discrete spin levels. For the sake of convenience, we define Δ_i as $(\varepsilon_i - \varepsilon_0)$, namely the energy gap between the energy level ε_i and the ground state ε_0. The definition of $\Delta_{1\text{–}7}$ is illustrated in fig. 2(f). The measured specific heat is fitted with the sum of eqs. (2) and (3). The lines of the best fit to the data for 0, 0.05, 0.5, 1, and 8 T are plotted in figs. 2(a)–(e). The Debye temperature obtained from the best fit is 185 ± 13 K, which cannot be determined precisely from the low-T specific heat only. But as shown in fig. 2, the two Schottky anomalies are dominant and affected very little by the cubic phonon component within this temperature range.

It has been reported that the two ground-state Kramer's doublets of V15 split by about 27 μeV even in the absence of an external magnetic field [10,19,20]. Two concepts were proposed to explain this zero-field splitting. The first one concerned the antisymmetric (AS) exchange interaction between the ions of the central triangle of V15 [16,19,21]. This AS exchange model successfully deduced the approximate expressions for energy levels in different ranges of the external field and provided a perfect fit to the staircase-like field dependence of magnetization of the V15 cluster at ultra-low temperatures. The second concept was based on the lattice distortion, which breaks the trigonal symmetry and introduces a splitting in the ground state. The inelastic neutron scattering (INS) study demonstrated that the low-energy properties of V15 are described by a triangle model with scalene distortion [20]. The ^{51}V nuclear magnetic resonance spectroscopy determined the local spin configuration and argued that the splitting originates from a distortion of the triangle from equilateral to nearly isosceles [22]. A Jahn-Teller structure deformation with a temperature-dependent splitting gap was considered theoretically to explain the lifting of its ground-state degeneracy without supposition of anisotropic exchange interactions in a V15 molecule [23,24].

Table 1: Energy gaps $\Delta_{1\text{–}7}$ of V15 obtained from the best fits to specific-heat data at 0, 0.05, 0.5, 1, and 8 tesla.

Field /T	Δ_1/meV	Δ_2/meV	Δ_3/meV	Δ_4/meV	Δ_5/meV	Δ_6/meV	Δ_7/meV
0	0.030(7)	–	–	0.349(12)	–	–	–
0.05	0.027(7)	0.010(10)	0.052(6)	0.339(11)	–	–	–
0.5	0.028(7)	0.070(8)	0.091(7)	0.291(13)	0.328(15)	0.403(15)	0.498(37)
1	0.027(3)	0.103(10)	0.126(9)	0.188(17)	0.340(15)	0.455(20)	0.584(40)
8	0.563(17)	0.605(21)	0.961(20)	1.459(35)	1.510(35)	1.878(70)	2.708(102)

Considering the corresponding thermal energies of the two Schottky anomalies, we assign Schottky 1 to the Schottky effect between the $S = 1/2$ Kramer's doublets, and Schottky 2 to the Schottky effect between the ground state and the $S = 3/2$ quartet states, respectively. A satisfying fit to Schottky 1 in the zero-field data requires two energy gaps, $\Delta_{ZF1} = 0.044(6)$ and $\Delta_{ZF2} = 0.016(7)$ meV, instead of one zero-field splitting as suggested in the aforementioned theories. We attribute the broadening of Schottky 1 to the level broadening produced by the interaction between the molecular spin and the nuclear spin bath in the system. This phenomenon in V15 has been first observed in field-dependent magnetization measurements when varying field sweeping rate and sample thermal coupling [11], and later evidenced by measuring the spin fluctuation down to 12 mK in muon spin-lattice relaxation measurements [25]. The broadening of the levels was reported to be a few tens of millikelvin. Unable to take this level broadening into account in the fit to specific-heat data, we determine the splitting of $S = 1/2$ Kramer's doublets by averaging Δ_{ZF1} and Δ_{ZF2}. The obtained splitting Δ_1 is 0.030 meV, consistent with the value determined by INS [20,26]. The broadening derived here matches those reported in [11] and [25] with an order of magnitude. In an external field of 0.05 T, Schottky 1 becomes broader and shows an increase in intensity. If we compare Schottky 1 in fig. 2(a) and (b), we can see it shifts towards lower temperatures when the external field is increased from 0 T to 0.05 T. This is indicative of an additional small energy gap (Δ_2) due to the Zeeman splitting of spin states $|0\ 1/2\ \pm 1/2\rangle$. But Δ_2 cannot be determined accurately at 0.05 T because nearly half of Schottky 1 is located below 70 mK. Schottky 2 at 0.05 T is fitted with a single energy gap Δ_4, because the Zeeman splitting of $S = 3/2$ quartet is much smaller than Δ_4 so that it cannot be resolved in terms of heat capacity. Note that in fig. 2(a) and (b) Schottky 2 is nearly identical. When the external field is increased to 0.5 T, the maximum of Schottky 1 is shifted to ~0.22 K owing to the Zeeman Effect of Δ_2 and Δ_3. At 1 T, the energy gaps from Δ_2 to Δ_7 give a joint, broad Schottky anomaly at ~1 K, leaving a clear evidence of the presence of Δ_1 by a small shoulder at ~0.1 K. The gap in the data for 1 T at ~1 K is due to an instrumental error where the specific heat suddenly dropped to zero. In the case of 8 T, there are deviations between the fit and the data below 0.7 K. Such deviations have also been observed in some other molecular magnetic systems [7,18,27], and are most likely due to the weak inter-molecule magnetic interactions, which were not considered in the theoretical models [7]. Another possible explanation is the residual entropy of the crystal water existing in these molecular magnets [18]. But as shown in fig. 2(e), such deviation (smaller than $0.1\,\mathrm{JK^{-1}mol^{-1}}$) is very weak and becomes relevant only at very low temperatures. The fitting results are summarized in table 1. The low-lying excitations determined in terms of heat capacity are in good agreement with the ones obtained by INS and theoretical model [16,20,26]. Note that the zero-field splitting of Kramer's doublets has been obtained indirectly in the INS experiment. Our heat capacity investigation provides valuable information of the low-lying energy spectrum of V15.

The temperature dependence of the magnetic entropy $S_\mathrm{m}(T, H)$ for a given applied field H can be obtained by integration of the experimental magnetic specific heat $C_\mathrm{m}(T)$, using

$$S_\mathrm{m}(T, H) = \int_0^T \frac{C_\mathrm{m}(T, H)}{T} \mathrm{d}T. \tag{4}$$

The MCE of V15 can then be evaluated by calculating the isothermal magnetic-entropy change $\Delta S_\mathrm{m}(T, \Delta H) = [S_\mathrm{m}(T, H_\mathrm{f}) - S_\mathrm{m}(T, H_\mathrm{i})]$ for a given field change of $\Delta H = H_\mathrm{f} - H_\mathrm{i}$. Since the experimental specific heat C_p could not be measured down to 0 K, the fitting results of the data for 0–1 T are extrapolated to 0 K to account for the region below 70 mK, while C_p for 8 T is extrapolated linearly to 0 K [28]. The contribution from the lattice specific heat is irrelevant, because it does not change with the field and therefore cancels out in the calculation of ΔS_m. The obtained temperature dependence of $-\Delta S_\mathrm{m}$ for several ΔH is shown in fig. 3(b). The maximum $-\Delta S_\mathrm{m}$ is reached at around 1.5 K for a field change of $\Delta H = (8 - 0.5)$ T, instead of for the maximum field change of $\Delta H = (8 - 0)$ T. The system shows mainly an inverse MCE within the field range of 0–0.5 T. The temperature dependence of $-\Delta S_\mathrm{m}$ plotted in fig. 3(c) is obtained without the extrapolation to 0 K. As can be seen in fig. 2, we could only measure part of Schottky 1 at low fields. Therefore, the $-\Delta S_\mathrm{m}$ in fig. 3(c) should be considered as a lower bound. For comparison, fig. 3(a) shows the theoretical magnetic-entropy change calculated from Hamiltonian (1).

Because the magnetic properties of V15 are governed by the central spin triangle at low temperatures, the

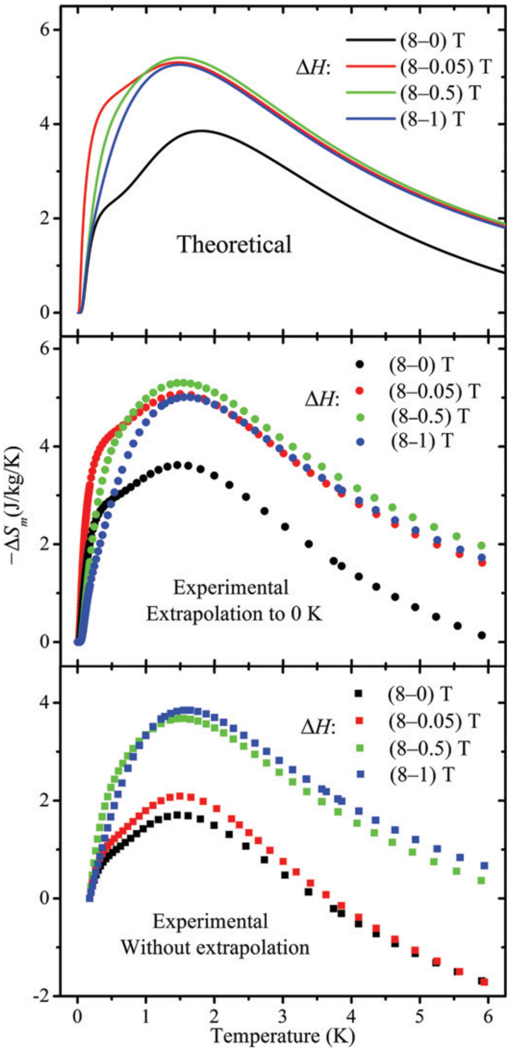

Fig. 3: (Colour on-line) Temperature dependence of the magnetic-entropy change $-\Delta S_{\mathrm{m}}$ of V15 for various field changes. (a) Theoretical calculation from Hamiltonian (1); calculation from data with (b) and without (c) extrapolation to $T = 0\,\mathrm{K}$.

maximum spin-only entropy change should correspond to $3R\ln(2s+1) = 2.08R = 7.37\,\mathrm{Jkg^{-1}K^{-1}}$ for $s = 1/2$. The maximum $-\Delta S_{\mathrm{m}}$ for $\Delta H = (8-0.5)\,\mathrm{T}$ is $5.31\,\mathrm{Jkg^{-1}K^{-1}}$ and smaller than the spin-only entropy. This is reasonable because the spins on the central triangle become uncoupled above 20 K [8]. However, it is worth noting that for $\Delta H = (8-0.05)\,\mathrm{T}$, $-\Delta S_{\mathrm{m}}$ increases sharply to $4.12\,\mathrm{Jkg^{-1}K^{-1}}$ as temperature increases from 0 to 0.4 K. This entropy change of $4.12\,\mathrm{Jkg^{-1}K^{-1}}$ is modest but it occurs at very low temperature. It is comparable to the $-\Delta S_{\mathrm{m}}$ of some high-spin sub-kelvin molecular refrigerants at ∼0.4 K [7,27,29,30], even though V15 possesses only a low-spin ground state ($S = 1/2$). A large-spin ground state is often favoured in the search of molecular coolers because the higher the spin value is, the larger the magnetic degrees of freedom and thus the larger the magnetic entropy. This impressive entropy change of V15 at 0.4 K is directly related to the zero-field splitting of the ground states. The anisotropy introduced by the AS exchange interaction or lattice distortion and the consequent zero-field splitting result in very-low-lying magnetic states, which then contribute to the magnetic entropy in ultra-low-T range. In the magnetic heat capacity, this corresponds to a peak close to $T = 0$. Such peak in magnetic specific heat has also been derived theoretically for spin-(1/2, 1) Ising chains and molecular magnets $\mathrm{Gd_4M_8}$ (M = Cu, Ni) [31,32]. Therefore, though zero-field splitting is not favoured in molecular refrigerants by the popular belief [33], it can still be useful in the design of sub-kelvin magnetic coolers. In spite of the low ground-state spin and zero-field splitting in V15, we have observed an average magnetocaloric capability of V15. It is also demonstrated that molecular magnets offer vast possibilities and significant advantages in the search of high-performance magnetic refrigerants due to their tuneable properties of spin, anisotropy, geometry, intra- and inter-molecular interactions.

Conclusion. – We have determined experimentally the low-lying magnetic excitations of V15 by analyzing the distinctive Schottky anomalies in specific heat measured down to 70 mK. The significant broadening of the Schottky anomaly at ∼0.1 K in zero magnetic field is attributed to the finite-energy level broadening produced by the interaction between the molecular spin and the nuclear spin bath. The resultant energy gaps show a rich picture of the low-lying energy levels of V15, giving strong support to the three-spin model, which is intended to explain the low-T magnetic properties of V15. The MCE of V15 is evaluated. In spite of the low-spin ground state, the entropy change of V15 at very low temperatures is comparable to that of some recently discovered sub-kelvin molecular coolers. The zero-field splitting of the ground states is responsible for this characteristic of V15 and could prove to be an advantage of molecular magnets in the field of sub-kelvin magnetic cooling.

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