Colossal refrigerant capacity in [Fe(hyptrz)₃]A₂ · H₂O around the freezing temperature of water

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We report a giant barocaloric effect in the spin-crossover compound [Fe(hyptrz)₃]A₂ · H₂O with hyptzr = 4-(3′-hydroxypropyl)-1,2,4-triazole and A = 4-chlorobenzenesulfonate. The origin of the giant barocaloric effect comes from the strong coupling between the lattice vibration and the electronic states $t_{2g}^6 (S = 0)$ and $(t_{2g}^4 e_g^2)(S = 2)$ of low and high spin in $Fe^{+2}N_6$ cores, respectively. Our theoretical and indirect experimental results lead to the barocaloric potential $\Delta S_T \sim 56$ J kg⁻¹ K⁻¹ and $\Delta T_{ad} \sim 10$ K, upon pressure changes $\Delta P = 0.9$ kbar, which can easily be obtained experimentally. The giant barocaloric in [Fe(hyptrz)₃]A₂ · H₂O leads to colossal refrigerant capacity of RC = 1223 J kg⁻¹ in a wide temperature span around ($T = 273$ K), the freezing temperature of the water.

I. INTRODUCTION

Presently, due to the strong necessity of saving energy consumption in cooling processes as well as finding new environmentally friendly refrigerant materials, several kinds of physical and chemical caloric effect are being thoroughly investigated [1,2]. In order to describe the caloric refrigeration potential of a solid material two thermodynamic quantities are usually computed: the entropy change in an isothermal process (ΔS_T) and the adiabatic temperature change (ΔT_{ad}), both calculated or measured upon applied external field variation (ΔF). Depending on the external field change, the caloric effects are termed as [3]: magnetocaloric ($\Delta F \rightarrow$ magnetic field change) [4,5]; electrocaloric ($\Delta F \rightarrow$ electrical field change) [6]; barocaloric and elastocaloric ($\Delta F \rightarrow$ hydrostatic pressure and uniaxial stress changes) [7–10]. In addition, the multicaloric effect [11] was named in the scenario where more than one type of caloric effects are coupled in multiferroic materials [12]. The area inside the rectangular $\Delta S_T \times \Delta T_{ad} = \Delta S_T \times (T_{hot} - T_{cold})$ isothermal-adiabatic-processes (Carnot cycle) is directly related with the work done, per cycle, to extract an amount of heat $\Delta S_T \times T_{cold}$ from the cold reservoir at temperature T_{cold} and reject an amount of heat $\Delta S_T \times T_{hot}$ into hot reservoir at temperature T_{hot}. Therefore, for good refrigerant materials we expected big reversible values of ΔS_T

and ΔT_{ad} in a wide temperature span and lower ΔF (which is directly associated with energy consumption).

In solid materials the barocaloric effect is expected to be relevant when an applied hydrostatic pressure change leads to a big volume variation and/or crystal symmetry change. Recently, Wu and coworkers reported a giant barocaloric effect in a MnCoGe₀.₉₉In₀.₀₁ compound involving orthorhombic-hexagonal magnetostructural transition around room temperature [13]. The coupling between magnetic and structural transition in MnCoGe around room temperature was achieved through replacing Ge by a small amount of In. The high values of $\Delta S_T = 52$ J kg⁻¹ K⁻¹ and $\Delta T_{ad} = 9.4$ K for pressure changes $\Delta P = 3$ kbar were obtained in the MnCoGe₀.₉₉In₀.₀₁ compound. More recently, García and coworkers reported a giant barocaloric effect around $T_C = 330$ K in [TPrA][Mn(dca)₃], where TPrA = (CH₃CH₂CH₂)₄N⁺ (tetrapropylammonium cation) and dca = [N(CN)₂]⁻ (dicyanamide anion) which belongs to the organic-inorganic hybrids group of the compounds [14]. This material presents strong influence of pressure on the first order phase transition temperature $\delta T_C / \delta P \sim 23$ K kbar⁻¹ (barocaloric coefficient). The physical origin of the giant barocaloric effect in [TPrA][Mn(dca)₃] comes from a complex first order structural phase transition involving a high configurational entropy change (~ 44 J kg⁻¹ K⁻¹) and very large cell volumetric deformation ($\Delta V / V \sim 1.25\%$) [15], leading to $\Delta S_T = 35.1$ J kg⁻¹ K⁻¹ at $T = 330$ K, upon $\Delta P = 0.0689$ kbar. Another giant barocaloric material that deserves to be highlighted is Gd₅Ge₂Si₂ [16] since this material was first achieved as a giant magnetocaloric material and is one of the most investigated and cited in the literature of caloric materials [17,18].

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In this paper we investigated the barocaloric effect in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O which belong to the so-called spin-crossover class of materials. Only recently, one of us predicted a giant value for the ΔS_T-barocaloric potential in this system from a microscopic theoretical model [19]. Nevertheless, as far as we know, the ΔT_{ad} investigation and comparisons of ΔS_T and ΔT_{ad} calculations with experimental data have not yet been done in spin-crossover materials. Very recently, some of us reported a proper Maxwell relation, connecting ΔS_T and ΔT_{ad} with the temperature derivative of the spin-crossover order parameter and the molecular volume change during the low spin (LS) to high spin (HS) phase transition process, which occurs in spin-crossover materials [20]. Basically, the huge barocaloric effect expected in spin-crossover systems comes from the three main contributions to the total entropy: (1) the electronic entropy; (2) the phonon entropy, and (3) the configurational entropy. For example, in iron (II) Fe^{+2}N$_6$ spin-crossover systems of octahedral coordination, the external pressure can changes the electronic HS-state configuration $(t_{2g}^4 e_g^2) - (S = 2)$ to LS state $t_{2g}^6 - (S = 0)$ leading to an electronic entropy contribution of $R \ln(2S + 1) \sim 13.4$ J mol^{-1} K^{-1}. However, due to the strong coupling between electronic and lattice vibration in spin-crossover systems, a giant entropy change (~ 80 J mol^{-1} K^{-1}) can be triggered by external pressure variation [21,22]. In this way, the main contribution comes from the phonon followed by electronic ones. The configurational entropy has a minority contribution in spin-crossover systems [20].

We report in this paper the giant barocaloric effect in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O, namely $\Delta S_T = 56$ J kg^{-1} K^{-1} and $\Delta T_{ad} = 10$ K, upon pressure change $\Delta P = 0.9$ kbar, from 4.1 to 5 kbar, leading to colossal refrigerant capacity of RC $= 1223$ J kg^{-1} around (273 K), the freezing temperature of water.

II. THEORY

Spin-crossover systems, formed by an ensemble of LS and HS molecules such as Fe^{+2}N$_6$ in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O [19] can be described by the microscopic Hamiltonian [20] which includes: (1) the intermolecular elastic interaction coupling; (2) elastic potential energy; (3) magnetic and phonons energy, and (4) crystalline electrical field interaction upon external pressure influence. From this Hamiltonian, in the mean field approximation, the following expression for the temperature and pressure dependence of entropy (per k$_B$-Boltzmann constant) can be obtained:

$$S(T, P) = -[\gamma_{HS} \ln(\gamma_{HS}) + (1 - \gamma_{HS}) \ln(1 - \gamma_{HS})]$$
$$+ \gamma_{HS}[\ln(5) + S_{HS}^{phon}] + (1 - \gamma_{HS})S_{LS}^{phon}, \quad (1)$$

where γ_{HS} is the molar fraction of HS molecules which can be calculated from the state equation:

$$\gamma_{HS} = \frac{1}{2}\left[1 + \tanh\left[\frac{2J(2\gamma_{HS} - 1) - \bar{\Delta} + k_B T \ln(g)/2}{k_B T}\right]\right]. \quad (2)$$

In the above equation $\bar{\Delta} = \Delta + P \delta V_{LH}/2$ is the Fe^{+2} d-orbital crystal field energy splitting, between t_{2g} and e_g or-

bitals, upon applied hydrostatic pressure, P, and δV_{LH} is the molecular volume change along the LS$\rightarrow$HS transition. $J = J_0 + J_1\omega$ is the elastic parameter coupling, with ω being the volumetric deformation of the octahedral Fe^{+2}N$_6$ molecular structure. This deformation depends on pressure and temperature through the relation [20] $\omega(T, P) = J_1(2\gamma_{HS} - 1)^2/\kappa V_{LS}$ where κ is the compressibility, and V_{LS} is the volume of molecules in the LS state ($\kappa V_{LS} = 10^3$ K is a typical value for spin-crossover materials [23]). S_{LS}^{phon} and S_{HS}^{phon} are, respectively, the LS and HS phonons entropy contribution in Fe^{+2}N$_6$ which depend on the vibrational molecular frequencies, ω_{LS} and ω_{HS}, as discussed in Ref. [20]. The parameter g in relation (2) accounts for the electronic and vibrational degeneracies of LS and HS states [20], and $k_B T$ is the thermal energy. The first term in relation (1) accounts for the LS and HS molecules configurational entropy and the second one comes from the coupling between the phonons and the spin-crossover order parameter γ_{HS}.

From a theoretical point of view, the barocaloric potential of a spin-crossover system, upon a pressure variation $\Delta P = P_2 - P_1$, can be calculated considering a pair of curves $S(T, P_1)$ and $S(T, P_2)$ from which the isothermal entropy changes $\Delta S_T(T, \Delta P)$ is directly calculated. To obtain the adiabatic temperature changes $\Delta T_{ad}(T, \Delta P)$ calculation, besides the entropy terms in relation (1), the Debye contribution (which is dependent only on temperature) should be added in order to account for the phonon contribution of all atoms, excluding the Fe^{+2}N$_6$ atoms already computed in relation (1).

Experimentally, ΔS_T and ΔT_{ad} can be indirectly measured through the proper established Maxwell relation for spin-crossover systems [20], namely,

$$\Delta S_T(T, P) = -\delta V_{LH} \int_{P_1}^{P_2} \frac{\partial \gamma_{HS}}{\partial T} dP, \quad (3)$$

and

$$\Delta T_{ad}(T, \Delta P) = \delta V_{LH} \int_{P_1}^{P_2} \left(\frac{T}{C_P}\right) \frac{\partial \gamma_{HS}}{\partial T} dP, \quad (4)$$

where C_P is the total heat capacity.

III. RESULTS AND DISCUSSION

In order to obtain the experimental results for the barocaloric effect in spin-crossover systems we need to obtain the pressure dependence of the molar fraction of HS molecules for several temperatures $\gamma_{HS}(P; T_i)$, $i = 1, 2...N$. This set of γ_{HS} vs P curves is then numerically integrated, using relations (3) and (4) which can be rewritten as

$$\Delta S_T(T, \Delta P) \approx -\frac{\delta V_{LH}}{\Delta T}\left[\int_{P_1}^{P_2} \gamma_{HS}(T + \Delta T) dP \right.$$
$$\left. - \int_{P_1}^{P_2} \gamma_{HS}(T) dP\right], \quad (5)$$

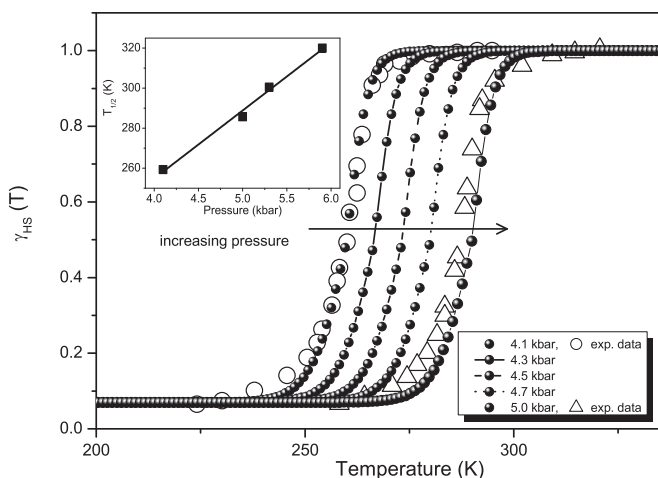FIG. 1. Temperature dependence of a molar fraction of HS molecules in [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$ H$_2$O upon several pressures. Open circles and triangles represent experimental data and the solid symbols represent the interpolated data. The inset shows the linear fitting of experimental data of T$_{1/2}$ vs P.

and

$$\Delta T_{ad}(T, \Delta P) \approx -\frac{\delta V_{LH}}{\Delta T}\left[\int_{P_1}^{P_2}\left(\frac{T}{C_P}\right)\gamma_{HS}(T + \Delta T)dP\right.$$
$$\left. - \int_{P_1}^{P_2}\left(\frac{T}{C_P}\right)\gamma_{HS}(T)dP\right]. \qquad (6)$$

It is worth noticing that for ΔT_{ad} determination, from relation (6), the temperature dependence of heat capacity should be previously determined. Since the investigation of the barocaloric effect in spin-crossover materials is just starting, it is not easy to find in the literature the set of curves $\gamma_{HS}(P; T_1, T_2, ...T_N)$ with low steps of temperature variations, ΔT, which are necessary to obtain accurate results from relations (5) and (6).

Figure 1 shows the experimental results for the temperature dependence of γ_{LS} in [Fe(hyptrz)$_3$]A$_2$ · H$_2$O [24]. Open circles and open triangles are experimental data obtained for $P = 4.1$ kbar and $P = 5$ kbar, respectively. The phase transition from LS to HS occurs at $\gamma_{LS}(T = T_{1/2}) = 1/2$. Therefore, the experimental transition temperatures are $T_{1/2} = 260$ and 287 K for $P = 4.1$ kbar and $P = 5$ kbar, respectively. In this way, as expected, the pressure stabilizes the LS phase since the crystalline electrical field splitting $\bar{\Delta}$ increases with pressure, overcoming the paring energy. The dotted curves represent our interpolation considering the phase transition temperature variation with pressure (barocaloric coefficient) $\delta T_{1/2}/\delta P = 33.2$ K kbar^{-1}. The inset shows the linear fitting of the experimental data of $T_{1/2}$ vs P extracted (from Fig. 1) in Ref. [24] (the low pressure point $P = 1$ bar, where hysteresis is present, was not included).

Figure 2 shows the pressure dependence of γ_{HS} for some temperature values between 260 and 290 K. These curves were obtained from a set of several curves of γ_{HS} vs T which were interpolated from experimental data (some interpolated curves are shown in Fig. 1, solid circles). The arrows indicate
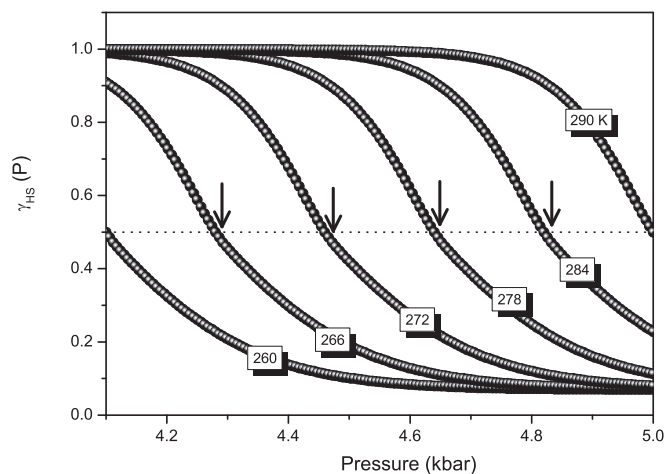

FIG. 2. Pressure dependence of the HS-molar fraction, γ_{HS}, in [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$ H$_2$O at different temperatures. The arrows indicate the spin-crossover phase transition critical pressure, $P_{1/2}$, for a given temperature.

the phase transition from low to high spin molecules defined as $\gamma_{HS}(P_{1/2}) = 1/2$ (dotted line). For a fixed pressure, when increasing temperature, we can observe that the high spin phase is stabilized. The mapping of γ_{HS} vs P from the isobaric γ_{HS} vs T curves is necessary in order to obtain the barocaloric quantities as formulated in relations (5) and (6). From Fig. 2 it is easy to note that the larger the area between two isothermal curves $\gamma_{HS}(T + \Delta T) - \gamma_{HS}(T)$, for a given temperature interval, the higher the values expected for the barocaloric effect, i.e., ΔS_T and ΔT_{ad} quantities. Also, the interval of γ_{HS}-pressure integration from P_1 to P_2 containing the critical temperature, $T_{1/2}$, should present maximum values for the ΔS_T and ΔT_{ad} thermodynamic quantities.

Figure 3 shows the ΔS_T vs T in [Fe(hyptrz)$_3$]A$_2$ · H$_2$O upon pressure variation from 4.1 to 5 kbar. The solid circles represent the indirect experimental data obtained from relation
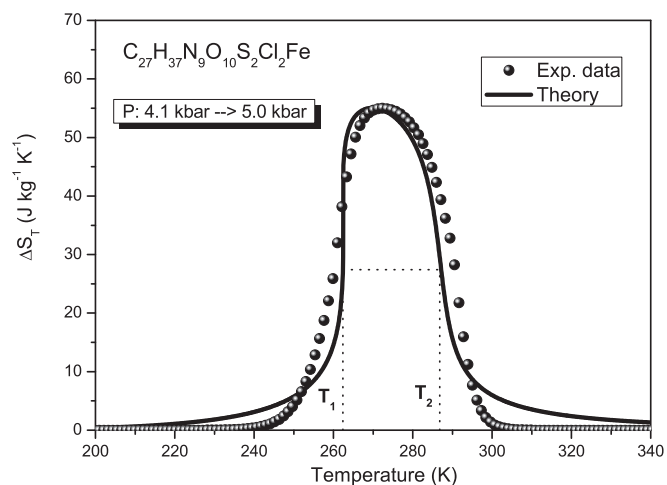

FIG. 3. Temperature dependence of isothermal entropy change, ΔS_T, in [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$ H$_2$O upon pressure changes from 4.1 to 5 kbar. The solid circles represent the experimental data and the curve comes from the calculations.

FIG. 4. Temperature dependence of the adiabatic temperature change, ΔT_{ad}, in [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$ H$_2$O upon pressure changes from 4.1 to 5 kbar. The solid circles represent the experimental data and the curve comes from the calculations. The ins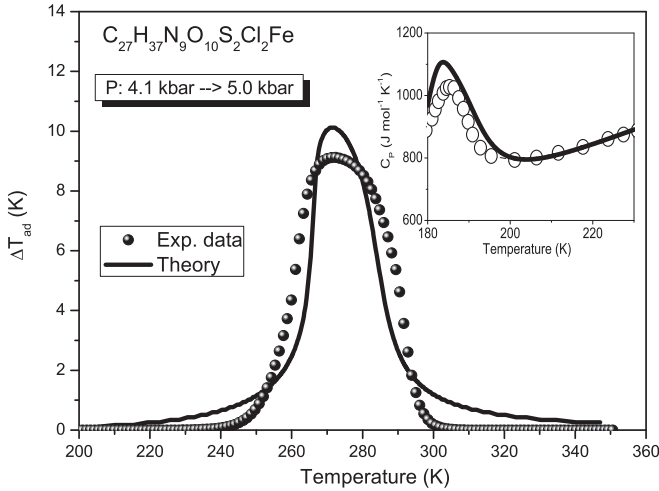et shows experimental data for the heat capacity vs temperature (open circles) and the curve comes from the calculation.

(5), considering $\Delta T = 0.5$ K as the temperature step. A very large barocaloric effect of 56 J kg^{-1} K^{-1} is achieved around 273 K. The solid curve represents the calculation adjusted using the model parameters: $J_0 = 33$ K, $J_1 = 75$ K, $\Delta = 645$ K, $\omega_{LS} = 285$ K and $\omega_{HS} = 190$ K. It is worth noticing that the distance between Fe-N decreases along the HS to LS phase transition, so the elastic force constant (associated to the Fe^{+2} harmonic vibration) increases which leads to $\omega_{LS} > \omega_{HS}$ which is well correlated with our adjusted parameters [25]. Since we did not found the volume change for the octahedral structure of Fe^{+2}N$_6$ in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O, we adopted the same value considered in [Fe(pzt)$_6$](PF$_6$)$_2$, namely $\delta V_{LH} = 28$ Å^3 [20]. The reduction of the Fe^{+2}N$_6$ octahedron volume from high to low spin electronic configuration is typically around 25% [26], for example, [Fe(phen)$_2$(NCS)$_2$] and [Fe(btz)$_2$(NCS)$_2$] have $\delta V_{LH} = 44$ and 47 Å^3, respectively [27,28]. The RC, defined as the integrated area under ΔS_T vs T curve in the limits T_1 and T_2 below the full width at half maximum [29], can be calculated leading to RC = 1223 J kg^{-1}.

It is important to compare our results for the barocaloric effect in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O with reported data for other barocaloric materials. For example, Gd$_5$Si$_2$Ge$_2$ which is considered a giant barocaloric compound [16] presents around $T_C = 260$ K maximum absolute values $\Delta S_T = 13$ J kg^{-1} K^{-1} (upon cooling) for pressure changes from 1 bar to 2.9 kbar, leading to RC = 133 J kg^{-1} and the barocaloric coefficient $\delta T_C / \delta P = 3.8$ K kbar^{-1}. The giant barocaloric material [TPrA][Mn(dca)$_3$] displays by direct measurement methods [14] $\Delta S_T = 35.1$ J kg^{-1} K^{-1} at $T = 330$ K, upon pressure change of 0.0689 kbar leading to RC = 62 J kg^{-1}. An important parameter that is directly related to the material refrigerant capacity is the barocaloric coefficient $\delta T_{1/2} / \delta P$, which measures the change of phase transition temperature upon pressure variation. As the $\delta T_{1/2} / \delta P$ parameter is large, so too

is the temperature interval computed in the RC calculation [see the $(T_2 - T_1)$ interval in Fig. 3]. For the above discussed materials we have: $\delta T_{1/2} / \delta P = 33.2$, 3.8, and 23 K kbar^{-1} for [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O, Gd$_5$Si$_2$Ge$_2$ and [TPrA][Mn(dca)$_3$], respectively.

Figure 4 shows the temperature dependence of the adiabatic temperature change in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O (molecular formula C$_{27}$H$_{37}$N$_9$O$_{10}$S$_2$Cl$_2$Fe) upon pressure variation from 4.1 to 5 kbar. The solid circles represent the indirect experimental data obtained from relation (6) and the solid curve represents the calculation through the microscopic model [20]. It is worth noticing that for the ΔT_{ad} vs T calculation, besides the phonon contribution of heat capacity from Fe^{+2}N$_6$, we should include the phonon contribution from the other ions components in [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O*which depend only on temperature*. This additional heat capacity, which is considered in the Debye assumptions, does not contributes to ΔS_T since it is calculated in isothermal processes. The inset in Fig. 4 displays the heat capacity as a function of temperature (C_P in J mol^{-1} K^{-1}), at ambient pressure, for our system (C$_{27}$H$_{37}$N$_9$O$_{10}$S$_2$Cl$_2$Fe). The open circles represent the experimental data [24] and the solid curve represents the calculation. In our investigated system the $\Delta T_{ad} = 10$ K maximum values upon pressure change $\Delta P = 0.9$ kbar occurs around 273 K in a wide interval of temperature ($\sim$28 K). For comparison, Gd$_5$Si$_2$Ge$_2$ presents $\Delta T_{ad} = 1$ K upon pressure change $\Delta P = 2$ kbar in a temperature interval of ($\sim$9 K) around 270 K [16].

IV. FINAL COMMENTS

In this paper the barocaloric effect, in both ΔS_T and ΔT_{ad} quantities, was reported from theoretical and experimental points of view in a spin-crossover material. The importance of γ_{HS} vs P isothermal curves and the δV_{LH} measurements in spin-crossover materials, in order to calculate the barocaloric effect, was highlighted. We also calculated the barocaloric potential in the [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O spin-crossover system upon the pressure variation $\Delta P = 0.9$ kbar. The interval of pressure change from 4.1 to 5 kbar was chosen due to (1) the available experimental data; (2) the absence of thermal hysteresis in γ_{HS} vs T curves; (3) the easy interpolation profile of γ_{HS} vs T experimental curves, and (4) the maximum caloric effect occurs around $T = 273$ K, the freezing temperature of water, which is suitable for technological refrigeration applications. The maximum barocaloric effects upon pressure change $\Delta P = 0.9$ kbar obtained for our system were $\Delta S_T = 56$ J kg^{-1} K^{-1} and $\Delta T_{ad} = 10$ K, leading to the colossal refrigerant capacity of RC = 1223 J kg^{-1} (about 10 times bigger than observed in giant barocaloric materials). In this way, our investigated system, [Fe(hyptrz)$_3$]A$_2 \cdot$ H$_2$O, can be considered as a potential giant refrigerant material to work in a solid state refrigerator.

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