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# A microscopic refrigeration process triggered through spin-crossover mechanism

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We report the giant barocaloric effect determined in a spin-crossover system using a microscopic model. Compared with the widely used gas compression-expansion refrigeration technology, field induced refrigeration in solid materials reduces environmental damages and improves the energy efficiency. The origin of the giant effect was ascribed to the entropic phonon contribution arising from low spin to high spin phase transition, induced by a pressure change. Here, we show that for the applied pressure variation from 1 bar to 4.1 kbar, the isothermal entropy change ($\Delta S_T$) in a one-dimensional spin crossover system [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$H$_2$O achieves a maximum value of 55.8 J mol$^{-1}$K$^{-1}$ at 191 K, leading to a huge refrigerant capacity of 2160 J mol$^{-1}$. Our results were compared with the results of other giant solid refrigerant materials such as (NH$_4$)$_2$SO$_4$, Gd$_5$Si$_2$Ge$_2$, and Gd$_5$[Si$_{0.43}$Ge$_{0.57}$]$_4$. *Published by AIP Publishing.*
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The potential of a solid refrigerant material is characterized by the isothermal entropy change $\Delta S_T$ upon controlled external field variations. If $\Delta S_T$ is obtained upon magnetic field variations, a magnetocaloric effect occurs; upon an electrical field change or a pressure change, electrocaloric or barocaloric effects occur, respectively.[1] Refrigerators based on solid refrigerant materials are energetically more efficient and environmentally friendly since they eliminate hazardous fluids.[2]

Many solid refrigerant materials, especially magnetocaloric materials, have been investigated from experimental and theoretical viewpoints.[3] The main drawbacks of solid refrigerant materials are associated with the hysteresis and high field change necessary to produce a considerable entropy change. The maximum entropy changes in usual magnetic materials are limited to the number of available magnetic states, given by the well know relation $\Delta S_T^{\max} = R\ln(2J + 1)$. For example, in a simple Gd ($J = 7/2$) compound, we expect $\Delta S_T^{\max} = 17.3$ J mol$^{-1}$ K$^{-1}$. However, several giant magnetocaloric materials were reported and their $\Delta S_T$-high values were ascribed to the coupling between magnetic and crystallographic phase transitions and deformations.[4–6]

The barocaloric effect was investigated in several works and materials, e.g., Pr$_x$La$_{1-x}$NiO$_3$ (Ref. 7) and ErCo$_2$ (Ref. 8), and the observed $\Delta S_T$-values were lower compared with their respective limits $R\ln(2J + 1)$. Recently, Lloveras and coworkers[9] reported giant barocaloric effects in ammonium sulphate [(NH$_4$)$_2$SO$_4$] of about $\Delta S_T^{\max} = 60$ J K$^{-1}$kg$^{-1}$ upon hydrostatic pressure variations $|P - P_{atm}| \approx 1$ kbar, leading to a refrigerant capacity of RC $= 276$ J Kg$^{-1}$. More recently, Sandeman reported the high barocaloric potential in spin crossover materials from the thermodynamic point of view.[10]

In this work, we focus on the iron (II) system of octahedral symmetry where transition occurs from the diamagnetic (S = 0) low spin (LS) state ($t_{2g}^6$) to paramagnetic (S = 2) high spin (HS) state ($t_{2g}^4 e_g^2$). In this process, a low magnetic entropy change is expected, $R\ln(2S + 1) \approx 13.4$ J mol$^{-1}$K$^{-1}$. However, a huge entropy change ($\sim$80 J mol$^{-1}$K$^{-1}$) can be triggered through the spin crossover transition process due to the activation of the vibrational (phonon) quantum states.[11,12] In this work, the barocaloric potential was investigated through the Ising-like microscopic model[13] with application to the one-dimensional spin crossover system [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$H$_2$O. This is an unusual system which presents several desired properties: (1) a very sharp transition from the LS to the HS state and vice-versa, (2) high pressure influence on phase transition temperature (dT$_C$/dP $= 240$ K(GPa)$^{-1}$), and (3) low applied hydrostatic pressure induces a parallel shift in the molar fraction curve-$\gamma_{HS}(T, P)$ from T $= 177$ K to above room temperature. Besides, low thermal hysteresis in this system is very important in order to reduce the energy loses in refrigeration cycles.[14,15]

The spin crossover system can be described by the Ising-like model Hamiltonian, first introduced by Wajnflaz and Pick.[16]

$$H = -h\sum_i \sigma_i - \sum_{\langle ij \rangle} \tilde{J}_{ij}\sigma_i\sigma_j + \frac{1}{2K}\omega^2 - P\omega, \quad (1)$$

where $\sigma_i$ denotes the fictitious spin which operates on HS and LS states, leading to $+1$ and $-1$ eigenvalues, respectively. $\tilde{J}_{ij}$ represents the intermolecular elastic interaction, coupling the (i) and (j)-molecules.[17] $h = \frac{k_BT}{2}\ln(g_{HS}/g_{LS}) - \Delta(P)$, with $k_BT$ being the thermal energy; $g_{HS}$ and $g_{LS}$ account for the degeneracies of HS and LS states[18,19] (for our calculation, we consider $\ln(g_{HS}/g_{LS}) = 6.9$ (Refs. 20 and 21); and $\Delta(P)$ is related to the crystalline electrical field energy gap between HS and LS states. This gap depends on the metal-ligand distance, and so, it is usually an increasing function of pressure.[22] $\omega$ is the volumetric deformation

(assumed homogeneous and isotropic), K is the compressibility, and P is the applied hydrostatic pressure (our Hamiltonian is in pressure units, i.e., energy per volume).

In order to describe the pressure influence on crossover materials, two order parameters are defined, namely, $\omega$ and $\gamma_{HS} = (1 + \langle\sigma\rangle)/2$ (the molar fraction of HS molecules; $\langle\cdots\rangle$ indicates the thermal average). The coupling between the order parameters is taken into account, considering the elastic interaction in the first order term of the Taylor series,

i.e., $\tilde{J} = J_0 + J_1\omega$. For a linear (1D) Ising model, an exact solution can be obtained for $\gamma_{HS}$ Ref. 12. However, in order to obtain expressions to describe (1D), (2D), and (3D) spin-crossover systems (without losing the general thermodynamic behavior of the linear system), we considered the Hamiltonian in molecular field approximation (MFA).[21] In MFA, embodying the number of first neighbors in the $\tilde{J}$ parameter, the $\gamma_{HS}$ state equation and the entropy are given by the following relations:

$$\gamma_{HS}(T,P) = \frac{1}{2}\left[1 + \tanh\left(\frac{2(2\gamma_{HS} - 1)(J_0 + J_1\omega) + (k_B T/2)\ln(g_{HS}/g_{LS}) - \Delta(P)}{k_B T}\right)\right], \qquad (2)$$

$$S(T,P) = R\left[\ln(2\cosh(x)) + \left[\frac{\ln(g_{HS}/g_{LS})}{2} - x\right]\right. \\ \left. \times (2\gamma_{HS} - 1) + \frac{\ln(g_{HS} \cdot g_{LS})}{2}\right], \qquad (3)$$

where R is the gas constant (the entropy was multiplied by the Avogadro number), $x$ is the same argument introduced into the *hyperbolic tangent* function in relation 2, and $\omega = K[P + J_1(2\gamma_{HS} - 1)^2]/2$ was obtained minimizing the Gibbs free energy. The $\langle\sigma\rangle^2$-dependence of the deformation can lead to a first order phase transition in the $\gamma_{HS}$-order parameter.[23] The relations (2) and (3) can be used to calculate the barocaloric potential $\Delta S_T = S(T, P_2) - S(T, P_1)$ in crossover materials, upon a pressure change $\Delta P = P_2 - P_1$ in an isothermal process.

Figure 1 shows the temperature dependence of $\gamma_{HS}$ in the one-dimensional polymeric spin crossover system [Fe(hyptrz)$_3$] (4-chlorophenylsulfonate)$_2$H$_2$O at different pressures: P = 1.0 bar, 4.1 kbar, and 5.0 kbar. The symbols represent the experimental data,[14,15] and the solid curves represent our simulations for *increasing temperature*. The calculation was performed using the adjusted model parameters: K = $10^{-3}$ (kbar)$^{-1}$, J$_0$ = 92 kbar, and J$_1$ = 260 kbar (for a scaling
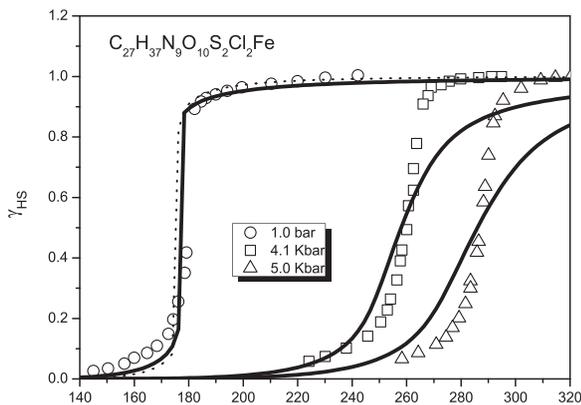
volume factor 0.14 Å$^3$, these values are similar to those reported by Gudyma *et al.*[21]). The energy gap was adjusted for each pressure $\Delta = 609$ kbar (P = 1.0 bar), 891 kbar (P = 4.1 kbar), and 988 kbar (P = 5.0 kbar). The high variation of $\Delta$, which is related to the crystal field, is supported in spin-crossover materials due to a large variation (up to about 10%), e.g., in the Fe-N bound length.[24] The pressure stabilizes the LS phase state since the decrease in the distance between Fe-N bound (increasing $\Delta$) and the electron-electron repulsion (which favor the HS phase), being an intra-atomic quantity, is rather insensitive to the lattice deformation. For P = 1 bar, $\gamma_{HS}$ *vs.* T curve shows a discontinuity around T = 178 K, indicating a first order phase transition process. The thermal hysteresis width of 4 K was calculated (see the dotted curve in Fig. 1, simulated upon *decreasing temperature*), and it is in good agreement with the measured experimental data, namely, 5 K, as discussed in Ref. 14. For P = 4.1 and 5.0 kbar, no thermal hysteresis is predicted in accordance with the experimental measurements at these pressures. However, the hysteresis width shows a non-monotonic character, i.e., it reappears above 5 kbar as experimentally reported in Ref. 14.

Figure 2 shows the temperature dependence of the entropy changes in isothermal processes upon applied pressure changes from P = 1.0 bar to 4.1 and 5.0 kbar and from P = 4.1 to 5.0 kbar (solid curves). The open circles[25] represent the barocaloric potential in Gd$_5$Si$_2$Ge$_2$ for applied hydrostatic pressure changes from 1 bar to 2.9 kbar, and the full circles represent the magnetocaloric potential in Gd$_5$[Si$_{0.43}$Ge$_{0.57}$]$_4$ for the applied magnetic field variation from zero to 5 T, Ref. 26. It should be highlighted that these Gd-Si-Ge systems are the examples of giant induced caloric effect materials due to the almost simultaneous magnetic and crystallographic phase transitions.[27] The squares represent some experimental data of the giant barocaloric material [(NH$_4$)$_2$SO$_4$] upon a pressure change $|P - P_{atm}| \approx 1$ kbar, from Ref. 9. Our results show huge $\Delta S_T$-values around 55.8 Jmol$^{-1}$K$^{-1}$ (or 66 JK$^{-1}$kg$^{-1}$ for our system C$_{27}$H$_{37}$N$_9$O$_{10}$S$_2$Cl$_2$Fe). The high $\Delta S_T$-values are observed in a large temperature range as is desirable for the tuning refrigeration process in a wide temperature interval. Usual magnetic refrigerant compounds have low limited values for the maximum entropy change associated with the number of available magnetic states. In addition, considerable



FIG. 1. Temperature dependence of the molar fraction $\gamma_{HS}$ in [Fe(hyptrz)$_3$](4-chlorophenylsulfonate)$_2$H$_2$O upon different applied pressures. The symbols represent the experimental data and solid curves represent our simulations for *increasing temperature*. The dotted curve was calculated for *decreasing temperature*.
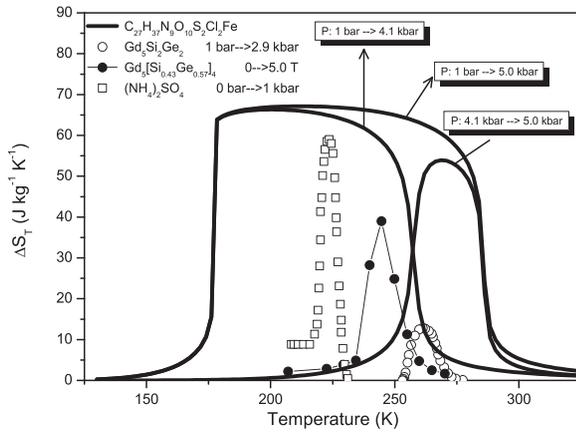
FIG. 2. Temperature dependence of isothermal $\Delta S_T$ calculated upon different pressure variations for the crossover material [Fe(hyptrz)$_3$] (4-chlorophenylsulfonate)$_2$H$_2$O (solid curves). For comparison, the giant barocaloric materials Gd$_5$Si$_2$Ge$_2$ (open circles) and [(NH$_4$)$_2$SO$_4$] (squares) and the giant magnetocaloric material Gd$_5$[Si$_{0.43}$Ge$_{0.57}$]$_2$ (full circles) were included.

$\Delta S_T$-values are observed in a sharp temperature interval around the magnetic phase transition. In a spin-crossover material, due to the large number of available states, we can achieve $\Delta S_T^{max} \approx 80 \, \text{J mol}^{-1} \text{K}^{-1}$ (which includes magnetic and phonon contributions).[11,12] Besides, the critical temperature $T_C$ ($\gamma_{HS}(T_C) = 1/2$) can be tuned with pressure in a wide temperature range (for $\Delta P : 1 \, \text{bar} \rightarrow 4.1 \, \text{kbar}$, we achieve $\Delta T \approx 80 \, \text{K}$). The refrigerant capacity (RC) is calculated by integrating the $\Delta S_T$ curve over the temperature range at half maximum. For $\Delta P : 1 \, \text{bar} \rightarrow 4.1 \, \text{kbar}$, we obtain 2160 J mol$^{-1}$, which is about 6 times larger than the value of 350 J mol$^{-1}$, reported for the giant caloric material Gd$_5$Si$_2$Ge$_{1.9}$Fe$_{0.1}$ (upon applied magnetic field variations from zero to 5 T).[28]

Next, we will describe the microscopic cooling process mechanism. For simplicity, the spin-crossover system with iron-II is represented by a FeN$_6$ core where Fe is centered in an octahedron upon the influence of an isotropic harmonic potential, as displayed in Figure 3. The harmonic potentials in HS and LS states are represented by parabolas $U(R) = \frac{m_S}{2} \omega_S^2 (R - R_S)^2 + U_0^S$, where $m_S$, $\omega_S$, and $U_0^S$ are the Fe-mass, frequency, and minimum potential in S = HS and LS states. The Fe ion in the two spin states has different vibrational frequencies ($\omega_{LS} > \omega_{HS}$) and Fe-N distances
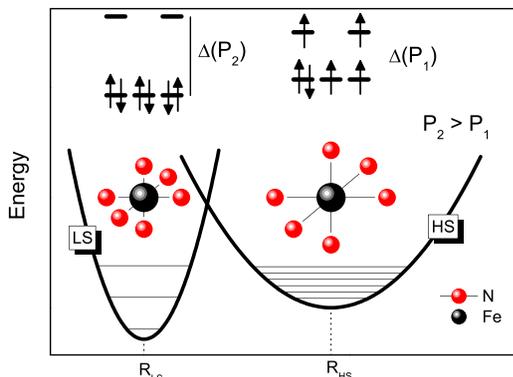
($R_{LS} < R_{HS}$). From quantum mechanics, the energetic distance between consecutive harmonic oscillator states is given by $\Delta \varepsilon_S = \hbar \omega_S$, leading to $\Delta \varepsilon_{LS} > \Delta \varepsilon_{HS}$. In addition, each vibrational excited energy level $\varepsilon_n = (n + 3/2)\hbar \omega_S$ is degenerate, and the degeneracy $g_S^{phon} = (n + 1)(n + 2)/2$ increases fast with energy. In this way, the HS and LS states present different values of vibration degeneracy ($g_{HS}^{phon} > g_{LS}^{phon}$), typically ($g_{HS}^{phon}/g_{LS}^{phon} \sim 1000$).[20] Besides different vibrational configurations, the HS and LS states present different spin states, namely, $t_{2g}^4 e_g^2$ (S = 2) and $t_{2g}^6$ (S = 0) for HS and LS states, respectively, as shown in Figure 3. Upon hydrostatic pressure variations from P$_1$ to P$_2$ (P$_2$ > P$_1$), an induced HS → LS phase transition (spin crossover) occurs (Fig. 3). The pressure decreases the Fe-N distance, increasing the crystalline electrical field interaction $\Delta(P_2) > \Delta(P_1)$, which overcomes the paring energy, leading to the LS configuration. Since the entropy is strongly correlated with the accessible quantum states, a huge entropy change can be obtained due to the LS → HS and LS → HS phase transitions, upon controlled pressure changes. The main contribution comes from different HS and LS-phonon spectra of energy, which is taken into account by the factor $\ln(g_{HS}/g_{LS})$, in our relation 3 (the spin and orbital degeneracies are also included in this factor).

Between two isobaric curves $S(T, P_1)$ and $S(T, P_2)$, a proper thermodynamic cycle can be considered for the refrigeration process, as fully discussed for magnetocaloric systems.[29] Investigations on spin-crossover materials may represent a major breakthrough in solid materials to be considered as refrigerant materials.

FIG. 3. Schematic representation of the electronic configurations and potential wells of Fe (II) (in FeN$_6$ octahedron) changes from the HS to the LS state upon pressure variations from P$_1$→P$_2$ (P$_2$ > P$_1$).

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