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Effect of Monovalent Doping on the Structural, Magnetic and Magnetocaloric Properties in $\text{La}_{0.7}\text{M}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ Manganese Oxides (M=Sr, Ba and M'=Na, Ag, K)

W. Cheikh-Rouhou Koubaa^{a,*}, M. Koubaa^a, A. Cheikhrouhou^{a,b}

^aLaboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B. P. 1171, 3000 Sfax, Tunisia

^bInstitut NEEL, CNRS, B.P.166, 38042 Grenoble cedex9, France

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Abstract

Structural, magnetic and magnetocaloric effects of powder perovskite manganites $\text{La}_{0.7}\text{M}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ (M=Sr, Ba and M'=Na, Ag and K) have been investigated. Our samples have been elaborated using the conventional solid state reaction at high temperature. X-Ray diffraction characterizations showed that all our synthesized samples crystallize in the distorted rhombohedral system with $R\bar{3}c$ space group. Magnetization measurements versus temperature in a magnetic applied field of 50mT showed that all our samples are ferromagnetic above room temperature. From the measured magnetization data of our synthesized samples as a function of magnetic applied field, the associated magnetic entropy change close to their respective Curie temperature T_C and the relative cooling power RCP have been determined. A maximum magnetic entropy change, $|\Delta S_M^{Max}|$, of $4.07\text{Jkg}^{-1}\text{K}^{-1}$ around 345K was obtained in $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample upon a magnetic field change of 5T. The $|\Delta S_M^{Max}|$ values of $\text{La}_{0.7}\text{Ba}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ are smaller in magnitude compared to $\text{La}_{0.7}\text{Sr}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ samples and occur at lower temperatures.

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Manganites; ferromagnetism; Curie temperature; Magnetocaloric effect

1. Introduction

The ABO_3 -type manganese oxides with general formula $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ where RE and AE, respectively, being a trivalent rare earth element and a divalent alkali-earth one have been extensively studied since the discovery in 1994 of a large magnetoresistance effect in these systems [1,2]. These materials exhibit many significant properties like metal-insulator transition, ferromagnetic-paramagnetic phase change, charge and orbital ordering, etc..., depending on several parameters as charge density, temperature, atomic structure, average ionic radius $\langle r_A \rangle$ of the A-site cations and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. Moreover, novel properties have been observed ten years ago in the perovskite-type

* Corresponding author. Tel./fax :+216 74 67 66 07.

E-mail address: wissem.koubaa@yahoo.fr.

ferromagnetic manganese oxides related to magneto-caloric effect [3,4]. The magnetocaloric effect was developed as a technology by Giauque and MacDougall [5] in 1933 in order to obtain very low temperatures (tenths of a Kelvin) using paramagnetic salt as a magnetic refrigerant. However, this cooling method has remained a low-temperature technique. Recently, there has been interest in extending the magnetic refrigeration technique to higher temperatures because of the desire to eliminate the chlorofluorocarbons present in high-temperature gas-cycle systems. Refrigeration in the sub-room temperature range is of particular interest due to the potential impact on energy savings as well as environmental concerns. Materials with large magnetocaloric effects are needed to improve energy efficiency. Pecharsky and Gschneidner [6,7] discovered a giant MCE in the pseudo-binary alloy $Gd_5(Si_xGe_{1-x})_4$ in the range of temperature from 50 to 280K. This is a great piece of work with enormous importance for both physics and technology. More recently, giant MCE at about 300 K has been measured in $MnFeP(O_{0.45}As_{0.55})$ [8]. Several studies have been published on magnetic perovskites for high-temperature magnetocaloric effect applications [9,10]. In the present work, we synthesized $La_{0.7}M_{0.2}M'_{0.1}MnO_3$ ($M=$ Sr, Ba and $M'=$ Na, Ag and K) powder perovskite manganites by the conventional solid state reaction at high temperature and studied the crystallographic, magnetic and magnetocaloric effects due to the substitution of 10% of strontium or barium by monovalent element Na, Ag and K.

2. Experimental techniques

Polycrystalline samples of $La_{0.7}A_{0.2}M_{0.1}MnO_3$ ($A=$ Sr, Ba and $M=$ Na, Ag and K) were synthesized using the solid state reaction method at high temperature. The starting materials were intimately mixed in an agate mortar and then heated in air up to 1000°C for 60h. The obtained powders were then pressed into pellets (of about 1mm thickness) and sintered at 1100°C in air for 60h with intermediate regrinding and repelling. Finally, these pellets were rapidly quenched to room temperature in air in order to freeze the structure at the annealed temperature. Phase purity, homogeneity and cell dimensions were determined by X-ray powder diffraction (XRD) at room temperature (diffractometer using Cu-K α radiation). Structural analysis was carried out using the standard Rietveld Method [11-12]. The Mn^{4+} ions amount has been quantitatively checked by iodometric titration. Magnetization measurements versus temperature in the range 20-400 K and versus magnetic applied field up to 7 T were carried out using a vibrating sample magnetometer. The $|\Delta S_M|$ induced by the magnetic field change have been determined from magnetization measurements versus magnetic applied field according to the classical thermodynamic theory based on Maxwell's relations.

3. Results and discussion

In our studied samples, the Mn^{4+} amount remains constant equal to 40%. Monovalent element doping leads to a change in the average ionic radius $\langle r_A \rangle$ and the mismatch size σ^2 of the A-cation site. The X-ray diffraction (XRD) patterns of all samples were recorded at room temperature. The XRD data refined using the Rietveld technique show that all our samples are single phase and can be indexed in the rhombohedral structure with $R\bar{3}c$ space group. A good fit between the observed and the calculated profiles was obtained, as shown in Fig. 1 for $La_{0.7}Sr_{0.2}Na_{0.1}MnO_3$ sample.

Fig. 2 displays the unit cell volume evolution versus $\langle r_A \rangle$ for both series. For $La_{0.7}Sr_{0.2}M_{0.1}MnO_3$ samples, we can observe that, with increasing $\langle r_A \rangle$, the unit cell volume is found to slightly decrease from 352.5Å³ for $M=$ Na to 351.1Å³ for $M=$ K, which can be explained by the increase of σ^2 . Whereas, in $La_{0.7}Ba_{0.2}M_{0.1}MnO_3$ compounds, the unit cell evolution is rather governed by $\langle r_A \rangle$ than σ^2 , which explain the observed increase of the unit cell volume. It should be noted that although both the A-site ionic radius and the mismatch size are similar for both $La_{0.7}Sr_{0.2}K_{0.1}MnO_3$ and $La_{0.7}Ba_{0.2}Na_{0.1}MnO_3$ samples, the unit cell volume presents different values. This behaviour emphasizes the effects of electronegativity difference between ions in A-site in our compounds [13]. With increasing $\langle r_A \rangle$, the Mn-O-Mn bond angle decreases from 166.7° for $La_{0.7}Sr_{0.2}Na_{0.1}MnO_3$ sample to 165.9° for $La_{0.7}Ba_{0.2}Na_{0.1}MnO_3$ sample while the Mn-O bond length increases from 1.957Å to 1.968Å, which influences the double exchange strength as will be discussed below.

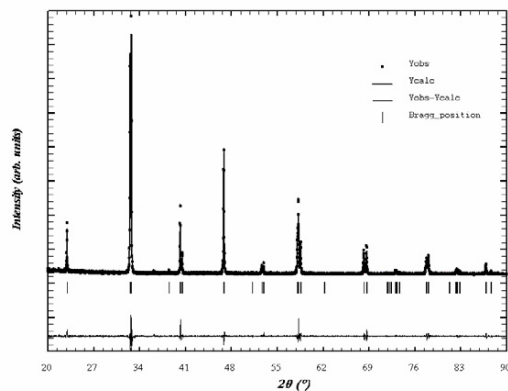


Fig. 1. X-Ray diffraction patterns at room temperature of $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample. Circles indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

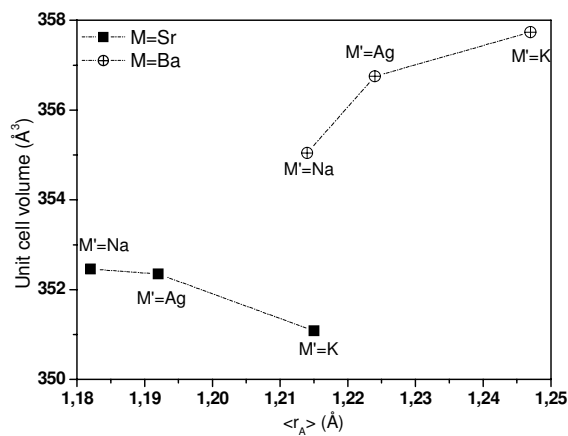


Fig. 2. Unit cell volume versus $\langle r_A \rangle$ for $\text{La}_{0.7}\text{M}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ ($M=\text{Sr}$, Ba and $M'=\text{Na}$, Ag and K) samples.

Magnetization measurements recorded versus temperature in the range 20–350K in a magnetic applied field of 50mT showed that all our substituted samples exhibit a sharp transition from paramagnetic to ferromagnetic phase with decreasing temperature, as illustrated in Fig. 3 for $\text{La}_{0.7}\text{M}_{0.2}\text{K}_{0.1}\text{MnO}_3$ ($M=\text{Sr}$, Ba) samples.

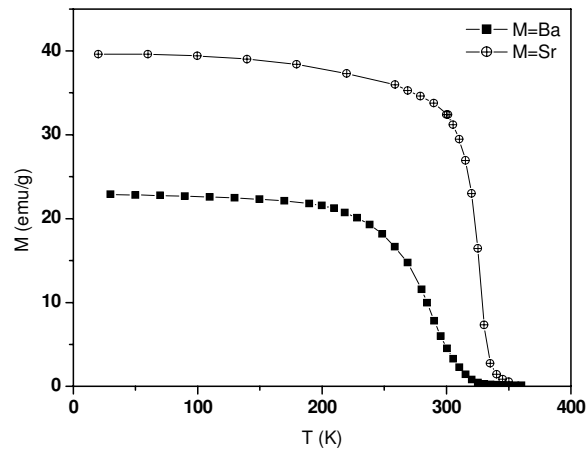


Fig. 3. Temperature dependence of magnetization at 50mT for $\text{La}_{0.7}\text{M}_{0.2}\text{K}_{0.1}\text{MnO}_3$ (M=Sr, Ba) samples.

The Curie temperature T_C has been taken as the position of the inflexion point in the $M(T)$ curves. As can be seen in Fig. 4, the Curie temperature shifts to lower values with $\langle r_A \rangle$ and varies from 340K for $\langle r_A \rangle = 1.182 \text{ \AA}$ to 311.5 K for $\langle r_A \rangle = 1.247 \text{ \AA}$.

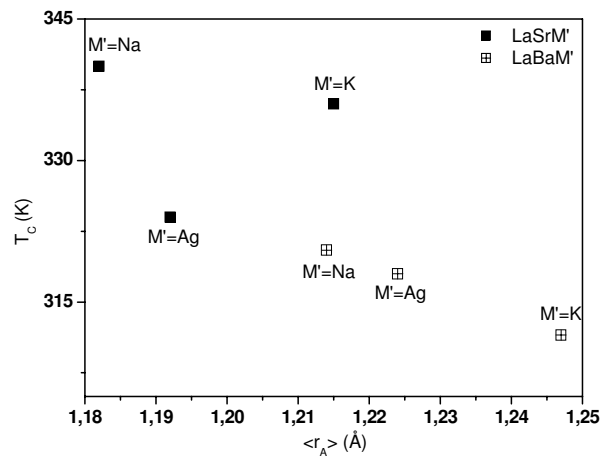


Fig. 4. Curie temperature versus $\langle r_A \rangle$ for $\text{La}_{0.7}\text{M}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ (M=Sr, Ba and $\text{M}' = \text{Na, Ag and K}$) samples.

The observed discrepancy between $\text{La}_{0.7}\text{Sr}_{0.2}\text{K}_{0.1}\text{MnO}_3$ and $\text{La}_{0.7}\text{Ba}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ compounds is also related to the effects of electronegativity difference between ions in A-site for the two samples. In order to confirm the ferromagnetic behavior of our samples at low temperatures, we performed magnetization measurements versus magnetic applied field up to 7T at several temperatures. A typical M(H) curves for $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample are plotted in Fig. 5.a).

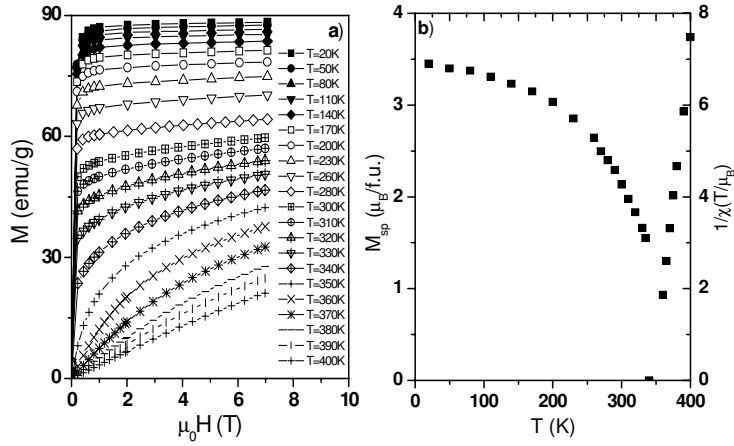


Fig. 5. a) Plot of magnetization M versus magnetic applied field μ_0H up to 7T at several temperatures and b) Temperature dependence of the spontaneous magnetization M_{sp} and $1/\chi$ for $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample.

Below T_C , the magnetization M increases sharply with magnetic applied field for $H < 0.5T$ and then saturates above 1T. The saturation magnetization shifts to higher values with decreasing temperature. This result confirms the ferromagnetic behavior of our sample at low temperatures. Fig. 5b shows the temperature dependence of the spontaneous magnetization M_{sp} and $1/\chi$ for $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample. The experimental value of the spontaneous magnetization $M_{sp}(\text{exp})$, deduced from the M(H) curves is found to be $3.48\mu_B/\text{Mn}$. The magnitude of the $M_{sp}(\text{exp})$ is comparable to the theoretical value of $3.6\mu_B/\text{mole}$ calculated for full spin alignment. The critical exponent γ defined by

$$M_{sp}(T) = M_{sp}(0) \left[1 - \frac{T}{T_C} \right]^\gamma \tag{1}$$

and deduced from the fit of the $M_{sp}(T)$ curve is found to be 0.31, which confirms the ferromagnetic behavior of our sample at low temperatures. The values of the spontaneous magnetization as well as the critical exponent are comparable for all our samples [14-16].

From the thermodynamical theory, the magnetic entropy change produced by the change of the magnetic field from 0 to H is given by [17]:

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left(\frac{\partial S}{\partial H} \right)_T dH \tag{2}$$

with Maxwell's relation

$$\left(\frac{\partial M}{\partial T} \right)_H = \left(\frac{\partial S}{\partial H} \right)_T \tag{3}$$

one can obtain the following expression:

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \tag{4}$$

According to (4) the maximum of the magnetic entropy change is attained at the Curie temperature T_C where the ferromagnetic-paramagnetic phase transition takes place. Using isothermal magnetization measurements in small discrete fields and temperature intervals, the magnetic entropy change can approximately be calculated using the numerical formula [18]:

$$\Delta S_M(T, H) = \sum_i \left(\frac{M_i - M_{i+1}}{T_{i+1} - T_i} \right) \Delta H_i \tag{5}$$

where M_i and M_{i+1} are the experimental magnetization values obtained at the temperatures T_i and T_{i+1} , respectively, in a magnetic applied field H_i . We plot in Fig. 6a the magnetic entropy change, $|\Delta S_M|$, of $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample as a function of temperature under several magnetic applied field changes. We observe that $|\Delta S_M|$ increases and reaches its maximum around the Curie temperature T_C . We can notice that the larger the magnetic applied field is, the larger the magnetic entropy change is obtained. The values of the maximum of the magnetic entropy change, $|\Delta S_M^{Max}|$, are 1.58, 2.34, 2.99, 4.07 and 4.99 J/kgK under magnetic applied field change of 1, 2, 3, 5 and 7 T, respectively.

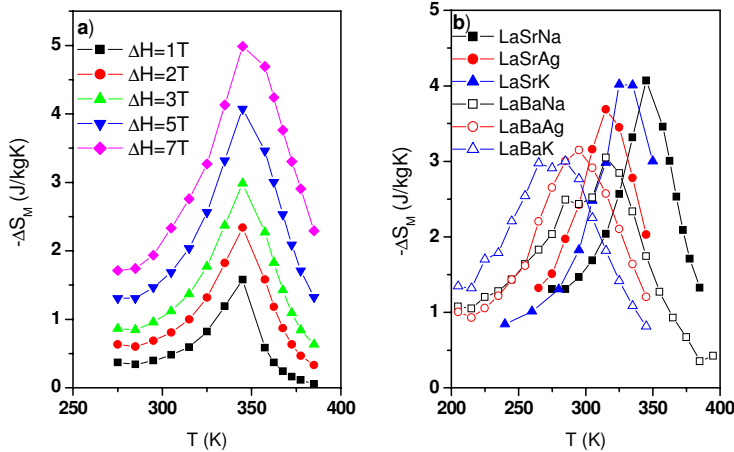


Fig. 6. a) Magnetic entropy change $-\Delta S_M$ evolution versus temperature at several magnetic applied field for $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample and b) Magnetic entropy change $-\Delta S_M$ evolution versus temperature at 5T for $\text{La}_{0.7}\text{M}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ samples ($M=\text{Sr, Ba}$ and $M'=\text{Na, Ag}$ and K).

We plot in Fig. 6b the different curves of the magnetic entropy change for all our synthesized polycrystalline samples as a function of temperature under 5T. For each series, the $|\Delta S_M^{Max}|$ values are comparable but the temperatures at which $|\Delta S_M^{Max}|$ occurs shift to lower values with increasing $\langle r_A \rangle$. The $\text{La}_{0.7}\text{Sr}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample exhibits the higher value of $|\Delta S_M^{Max}|$, 4.07 J/kg $^{-1}\text{K}^{-1}$, around 345K. For $\text{La}_{0.7}\text{Ba}_{0.2}\text{Na}_{0.1}\text{MnO}_3$ sample, we observe an asymmetrical broadening of $|\Delta S_M|$ peak, which can be explained by structural inhomogeneity. Although these $|\Delta S_M^{Max}|$ values in our samples are smaller than that observed in Gd or Gd-based compounds, the $|\Delta S_M|$ versus temperature curves are significantly broader. This wider temperature range with large magnetic entropy change is useful for an ideal Ericsson refrigeration cycle. Moreover, our samples are interesting in application as potential

candidates in magnetic refrigeration since they are cheap, easier to fabricate, possess tunable T_C and high chemical stability.

In the magnetic refrigeration technology, it is of utmost interest that the magnetocaloric effect extends over a large temperature range; we can then consider the relative cooling power (RCP) given by [19]

$$RCP = -\Delta S_M(T, H) \times \delta T_{FWHM} \quad (6)$$

where δT_{FWHM} is the full-width at half-maximum of $|\Delta S_M|$ versus temperature and $|\Delta S_M^{Max}|$ is the maximum of $|\Delta S_M|$. For $\text{La}_{0.7}\text{Sr}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ samples, the RCP values for $\text{M}'=\text{Na}$, Ag and K are respectively 118.4, 116.6 and 121.1 J/kg at 5T. These values are comparables and lower than that observed in $\text{La}_{0.7}\text{Ba}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ samples. The RCP values are found to be 307.1 J/kg, 271 J/kg and 337.9 J/kg at 5T for $\text{M}'=\text{Na}$, Ag and K respectively although these samples present $|\Delta S_M^{Max}|$ values much smaller. This result confirms that the larger the δT_{FWHM} the better the cooling capacity. Fig. 7 illustrates these RCP values as a function of T_C for both series upon a magnetic field change of 5T in comparison with Gd metal which is considered as the most active refrigerant near room temperature.

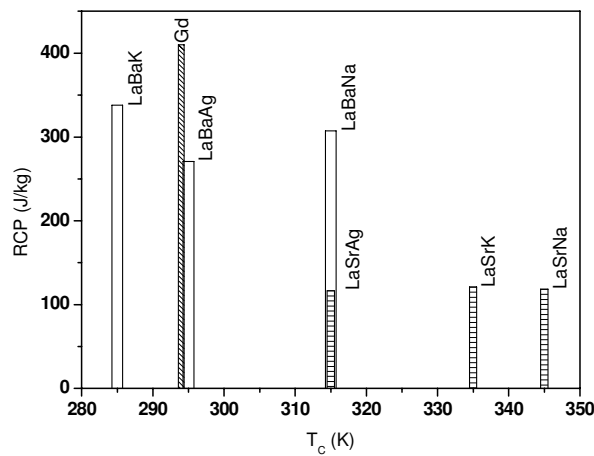


Fig. 7. RCP values versus T_C for $\text{La}_{0.65}\text{Ca}_{0.3}\text{M}'_{0.05}\text{MnO}_3$, $\text{La}_{0.65}\text{Ba}_{0.3}\text{M}'_{0.05}\text{MnO}_3$ and Gd

We can also notice that the RCP value of $\text{La}_{0.7}\text{Ba}_{0.2}\text{K}_{0.1}\text{MnO}_3$ sample is higher in magnitude and occurs close to room temperature compared to $\text{M}'=\text{Na}$ and Ag samples. In addition the magnitude of the RCP is about 82% of that of pure Gd.

4. Conclusions

We investigated the effect of monovalent doping on the physical properties of $\text{La}_{0.7}\text{M}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ ($\text{A}=\text{Sr}$, Ba and $\text{M}'=\text{Na}$, Ag and K) powder samples. The structural study shows that all our synthesized samples crystallize in the rhombohedral structure with $R\bar{3}c$ space group. All our samples exhibit a paramagnetic-ferromagnetic transition with decreasing temperature. A large magnetocaloric effect above room temperature is observed in all our samples. In this study, we have shown that $\text{La}_{0.7}\text{Sr}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ compounds exhibit the larger $|\Delta S_M^{Max}|$ values above room temperature; however they are less interesting for technological applications than $\text{La}_{0.7}\text{Ba}_{0.2}\text{M}'_{0.1}\text{MnO}_3$ samples presenting higher RCP values near 300K. A mixture of the three latter compounds characterized by slightly different

transition temperatures could result in a more broadened magnetic entropy curve leading to an active magnetic refrigerator.

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