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# Relative cooling power modeling of lanthanum manganites using Gaussian process regression

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Efficient solid-state refrigeration techniques at room temperature have drawn increasing attention due to their potential for improving energy efficiency of refrigeration, air-conditioning, and temperature-control systems without using harmful gas in conventional gas compression techniques. Recent developments of increased magnetocaloric effects and relative cooling power (RCP) in ferromagnetic lanthanum manganites show promising results of further developments in magnetic refrigeration devices. By incorporating chemical substitutions, oxygen content modifications, and various synthesis methods, these manganites experience lattice distortions from perovskite cubic structures to orthorhombic structures. Lattice distortions, revealed by changes in lattice parameters, have significant influences on adiabatic temperature changes and isothermal magnetic entropy changes, and thus RCP. Empirical results and previous models through thermodynamics and first-principles have shown that changes in lattice parameters correlate with those in RCP, but correlations are merely general tendencies and obviously not universal. In this work, the Gaussian process regression model is developed to find statistical correlations and predict RCP based on lattice parameters among lanthanum manganites. This modeling approach demonstrates a high degree of accuracy and stability, contributing to efficient and low-cost estimations of RCP and understandings of magnetic phase transformations and magnetocaloric effects in lanthanum manganites.

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### 1 Introduction

Energy efficiency and sustainability are priority topics in modern society. Refrigeration and air conditioning account for a significant amount of power consumption among various end uses of energy in both commercial and residential areas.10 Most refrigeration technology relies on the conventional gas compression (CGC) technique, which has drawn increasing criticisms due to its lack of efficiency and use of air-pollutant gas. Recent developments of magnetic refrigeration (MR) technology, based on the magnetocaloric effect in magnetic materials particularly near room temperature, have offered an exciting alternative to vapor compression refrigeration.20 Advantages of MR technology over CGC include, but not limited to, almost ten-fold higher cooling efficiency in magnetic refrigerators, much smaller footprints, complete solid-state operation, and being environmentally friendly.21 Furthermore, recent developments in high-temperature superconductors with enhanced critical temperature and magnetic fields that can be generated have prompted developments of high-efficiency MR devices with superconducting magnetic field sources. 8,22,28-30 An early development of a gadolinium (Gd) rare earth metal with a large magnetocaloric effect (MCE) marked

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a significant starting point in developing room-temperature MR, but its application in large-scale commercial usage was greatly limited due to the very high price of Gd.9 Therefore, numerous research has been conducted to search for new materials with large MCEs, large relative cooling power (RCP), and cheap prices.

Among these materials, ferromagnetic lanthanum manganites, with the general formula,  $La_{1-x-y}RE_xA_yMn_{1-z}TM_zO_3$ where RE is a rare earth element that partially or totally substitutes lanthanum, A is an element of the IA or IIA group, and TM is a transition element that partially substitutes Mn, are of practical importance. These materials have unique properties such as small magnetic and thermal hysteresis, a large MCE around Curie temperature  $T_{\rm C}$ , and a broad working temperature range. Furthermore, manganites are inexpensive to prepare, chemically stable, and highly electrically resistive.6 The parent LaMnO<sub>3</sub> compound is semiconducting and orders antiferromagnetically at 150 K, but a formation of mixed valence in Mn ions via a double exchange mechanism between Mn<sup>4+</sup> and Mn<sup>3+</sup> can induce ferromagnetism. A wide range of  $T_{\rm C}$  from  $\sim$ 150 K to 375 K can be obtained by, for example, substitution of a divalent ion  $(Ca^{2+}, Ba^{2+}, Sr^{2+}, etc.)$  or a monovalent ion  $(Na^{1+}, K^{1+}, etc.)$  for La<sup>3+</sup>, and an excess of oxygen. Furthermore, the ground state of manganites can be tuned by partial substitution of La3+ by a trivalent rare earth, or in a La-free Pr or Nd manganites. These perovskite-based structures show lattice distortions as a result

 $\begin{tabular}{ll} \textbf{Table 1} & \textbf{Experimental data and relative cooling power predictions}^a \end{tabular}$ 

Lia, Chi, Mitto)         5.902         7.771         5.340         9.67         9.79         9.79         9.89         9.80<	Sample	a (Å)	<i>b</i> (Å)	c (Å)	Experimental relative cooling power (J $\mathrm{kg}^{-1}$ )	Predicted relative cooling power (J $kg^{-1}$ )	Reference	Magnetic property
5.4588         7.6741         5.4383         9.72         9.87         25           5.4588         7.6741         5.4383         9.72         9.87         4           5.4813         7.6853         5.4519         62.00         98.7         4           5.4813         7.6853         5.4519         62.00         62.02         17           5.4813         7.6921         5.4519         62.00         88.02         18           5.5419         7.6921         13.00         13.00         13.00         13.00           5.5486         7.700         5.4663         13.00         17.01         13           5.5060         7.7866         5.525         17.00         175.01         13           5.4384         5.4627         18.00         175.01         13           5.4384         5.4627         18.00         175.01         13           5.4384         5.4627         18.00         175.01         13           5.4384         5.4640         18.00         175.01         13           5.4384         5.4640         18.00         24.00         13           5.4387         5.4480         2.450         2.20         2.20	$\mathrm{La_{0.8}Ca_{0.2}MnO_3}$	5.4972	7.7771	5.5149	3.67	3.70	13	2nd order FM-PM transition
5.458         7.6741         5.430         10.00         9.87         4           5.413         7.6741         5.430         10.00         6.402         6.202         18           5.413         7.691         5.4608         88.00         123.01         18           5.413         7.6921         5.4608         13.00         123.01         18           5.523         7.7200         5.463         113.00         147.01         17           5.5266         7.734         5.604         183.00         175.01         13           5.5265         7.734         5.604         183.00         147.01         17           5.4066         7.734         5.604         183.00         183.20         13           5.4380         7.738         5.476         120.00         192.01         13           5.4381         7.7582         2.436         2.200         190.01         14           5.4382         5.439         2.000         2.200         14           5.4382         5.4462         2.200         2.200         14           5.4382         5.4462         2.600         2.200         2.4600         14           5.4382	$Pr_{0.7}Ca_{0.3}MnO_3$	5.4598	7.6741	5.4303	9.72	9.87	25	2nd order FM-PM transition
54813         76853         54519         6200         6202         18           54814         76853         54519         6200         6200         6200         18           55032         77200         5469         123.00         133.01         13           55032         77200         5469         123.00         175.01         18           55036         7780         5525         179.00         175.01         13           5506         7786         183.00         183.51         13           5506         7786         183.00         183.51         13           5506         7786         183.50         183.51         13           5439         7653         5469         183.00         183.51         13           5438         5463         7670         183.50         13         13           5439         7669         220.00         246.39         14         14           5423         7669         220.00         230.01         14         14           5423         7669         220.00         230.01         14         14           5423         5463         2460         220.00	Pr <sub>0.7</sub> Ca <sub>0.3</sub> MnO <sub>3</sub>	5.4598	7.6741	5.4303	10.00	9.87	4	2nd order FM-PM transition
5.419         7.6921         5.4608         88.00         17.0           5.5435         7.6921         5.460         123.00         13.0         13.0         117.01         18           5.5486         7.700         5.4673         147.00         147.01         13         18           5.5486         7.700         5.4673         147.00         147.01         13           5.506         7.7347         5.584         183.00         179.01         13           5.506         7.7348         5.4380         7.6776         192.03         193.03         193.03           5.4349         7.6776         192.00         192.01         13         14           5.4384         5.4380         7.6786         22.00         26.03         23           5.4383         7.6786         2.20.00         23.00         14         14           5.4382         7.7589         5.4562         22.00         246.00         14         14           5.4382         7.6475         2.00.00         2.30.00         240.00         14         14         14         14         14         14         14         14         14         14         14         14	$La_{0.6}Pr_{0.1}Ba_{0.3}Mn_{0.7}Ni_{0.3}O_3$	5.4813	7.6853	5.4519	62.00	62.02	18	2nd order FM-PM transition
5,500.2         7,7200         5,4690         123.00         113.01         118           5,505.3         7,7200         5,4750         147.00         147.01         175.01         175.01           5,505.3         7,7800         5,535.3         147.00         147.01         175.01         175.01           5,505.0         7,7866         5,535.3         199.00         183.02         13           5,506.0         7,7866         5,535.2         199.00         183.02         13           5,4834         7,673         5,4646         183.50         183.22         23           5,4834         7,6781         2,4870         2,200.01         192.01         14           5,4834         5,4846         2,4850         2,20.00         2,20.00         18           5,501         7,7538         5,4850         2,20.00         2,20.00         14           5,4825         5,4827         7,6739         2,40.00         2,40.00         14           5,4827         5,4829         7,6773         2,40.00         2,40.00         14           5,4827         5,4427         7,6800         2,58.00         2,40.00         14           5,4427         5,4415	${\rm La_{0.67}Ca_{0.33}Mn_{0.75}Cr_{0.25}O_3}$	5.4419	7.6921	5.4608	88.00	88.02	17	2nd order FM-PM transition
5,4486         7,7000         5,4673         147,00         147,01         175,01<	$La_{0.6}Pr_{0.1}Ba_{0.3}Mn_{0.9}Ni_{0.1}O_{3}\\$	5.5032	7.7200	5.4690	123.00	123.01	18	2nd order FM-PM transition
5.22.53         7.8002         5.515.2         175.00         175.01         13           5.506         7.7866         5.2255         175.00         175.01         13           5.506         7.7866         5.2255         175.00         183.70         183.70         13           5.436         7.786         192.00         192.01         13         14           5.438         7.678         219.03         219.03         16           5.438         7.689         222.78         226.00         16           5.438         7.7368         220.00         226.00         16           5.4482         5.4387         7.6773         240.00         226.00         18           5.4482         5.4489         7.6773         240.00         230.01         16           5.4482         7.6460         228.00         228.00         16           5.4482         7.6473         240.00         242.00         17           5.4482         7.6460         242.00         242.00         11           5.4482         7.6461         242.00         242.00         242.00           5.4482         7.6461         268.00         226.00         11	${\rm La_{0.67}Ca_{0.33}Mn_{0.9}Cr_{0.1}O_3}$	5.4486	7.7000	5.4673	147.00	147.01	17	2nd order FM-PM transition
5.5050         7.7866         5.2255         179,00         179,01         13           5.5066         7.7866         5.2255         179,00         183,01         13           5.4019         7.6734         5.5084         183,00         183,01         13           5.4334         5.4624         7.6776         192,00         219,201         213           5.4334         5.4884         7.6738         5.4862         2.22.78         246.30         2.3400         16           5.4338         7.6738         5.4862         2.22.00         220.00         23         23           5.5121         7.7508         5.4876         2.22.00         20         20         16           5.4028         7.6739         2.20.00         220.00         16         43         16           5.412         7.6739         2.4200         2.40.00         240.00         16         16           5.418         7.673         2.4120         7.6730         2.42.00         2.42.00         11           5.4417         7.661         2.5519         2.42.00         2.42.00         2.42.00         11           5.4417         7.661         2.5600         2.22.30         2.	$\mathrm{La_{0.8}Ca_{0.05} \square_{0.15}MnO_{3}}$	5.5253	7.8002	5.5152	175.00	175.01	13	2nd order FM-PM transition
5.6066         7.7937         5.6084         183.00         183.01         183.01         133.52         23           5.4384         5.4646         183.50         183.52         23           5.4384         5.4638         7.6778         219.03         192.01         14           5.4384         5.4638         7.6738         222.73         246.39         2.6           5.4384         7.7388         5.4456         226.00         226.00         1           5.5121         7.7388         5.4459         220.00         220.00         1           5.4482         5.4387         7.6779         230.01         230.01         16           5.4482         5.4387         7.6779         240.00         233.00         14           5.4482         5.4489         7.6773         240.00         233.00         14           5.4482         5.4489         7.6773         240.00         242.00         14           5.4482         5.4499         7.6773         240.00         242.00         14           5.4417         7.7601         255.00         242.00         14         14           5.4417         7.641         243.00         242.00         1	$\mathrm{La_{0.8}Ca_{0.1} \square_{0.1}MnO_{3}}$	5.5050	7.7866	5.5255	179.00	179.01	13	2nd order FM-PM transition
5.4319         7.6753         5.4646         183.50         183.52         23           5.4334         5.4624         5.4624         1.92.00         192.01         14           5.4333         5.4380         7.6776         192.00         219.03         219.03           5.4333         7.489         5.452         222.78         246.39         23           5.5121         7.7368         5.489         230.01         18           5.4387         7.673         230.01         230.01         18           5.4387         7.6830         23.00         230.00         18           5.4382         5.439         7.673         240.00         240.00         16           5.4482         5.4490         7.673         240.00         240.00         16           5.4482         5.4429         7.6800         242.00         11           5.4482         5.4420         7.6810         256.00         243.00         11           5.4417         5.4691         2.68.00         243.00         11           5.4427         5.4449         7.6800         26.20         240.00         11           5.4427         5.4410         7.6800         26.20 </td <td><math>\mathrm{La_{0.8}Ca_{0.15} \square_{0.05}MnO_{3}}</math></td> <td>5.5066</td> <td>7.7937</td> <td>5.5084</td> <td>183.00</td> <td>183.01</td> <td>13</td> <td>2nd order FM-PM transition</td>	$\mathrm{La_{0.8}Ca_{0.15} \square_{0.05}MnO_{3}}$	5.5066	7.7937	5.5084	183.00	183.01	13	2nd order FM-PM transition
5.4884         5.4624         7.6776         192.00         192.01         14           5.4383         5.4864         7.6776         190.03         116         16           5.4383         7.6691         7.4786         222.78         246.39         23           5.5038         7.7388         5.4746         226.00         226.00         18           5.4823         5.4829         7.6839         233.00         14         16           5.4824         5.4329         7.6830         240.00         240.00         14           5.4825         5.4429         7.6803         241.20         240.00         14           5.4825         5.4429         7.6804         240.00         240.00         14           5.4825         5.4429         7.6803         240.00         240.00         14           5.4826         5.4429         7.6804         256.00         11           5.4827         5.4469         7.6800         258.00         14           5.4827         5.4469         7.6800         258.00         14           5.437         5.4469         2.68.00         268.00         14           5.4427         5.4469         2.68.00 <td><math>Pr_{0.7}Ca_{0.3}Mn_{0.9}Fe_{0.1}O_3</math></td> <td>5.4319</td> <td>7.6753</td> <td>5.4646</td> <td>183.50</td> <td>183.52</td> <td>23</td> <td>2nd order FM-PM transition</td>	$Pr_{0.7}Ca_{0.3}Mn_{0.9}Fe_{0.1}O_3$	5.4319	7.6753	5.4646	183.50	183.52	23	2nd order FM-PM transition
5.4333         5.4880         7,6786         219,03         219,03         116           5.4293         7,6891         5,436         222,78         246,39         23           5.5038         7,7888         5,4456         222,78         226,00         1           5.5121         7,7508         5,4859         230,00         230,00         1           5.4823         5,4397         7,6773         240,00         240,00         14           5.4835         5,4439         7,6773         240,00         240,00         14           5.4837         7,6791         240,00         240,00         16           5.4837         7,6814         243,00         241,20         16           5.4837         7,6814         243,00         241,20         11           5.4837         7,6814         243,00         246,00         11           5.4847         7,6814         243,00         265,00         11           5.4427         7,4415         7,6814         265,00         266,20         11           5.4427         7,441         266,20         266,20         11           5.4417         7,641         266,20         266,20         11	$Pr_{0.6}Ca_{0.1}Sr_{0.3}Mn_{0.975}Fe_{0.025}O_{3}\\$	5.4384	5.4624	7.6776	192.00	192.01	14	2nd order FM-PM transition
5.4938         7.4691         5.4552         222.78         246.39         23           5.5038         7.7388         5.4846         220.00         226.00         11           5.5131         7.7388         5.4849         220.00         230.00         18           5.4823         5.4837         7.6779         230.00         230.00         16           5.4824         5.4839         7.6779         230.00         230.00         16           5.4825         5.4429         7.6773         241.20         241.20         16           5.4825         5.4429         7.6814         242.00         241.20         16           5.4827         5.4429         7.6819         242.00         241.20         11           5.4427         7.6441         266.00         242.00         11           5.4427         7.6441         266.00         256.00         11           5.4427         7.4450         7.6441         266.00         266.00         11           5.4427         7.4450         7.6441         266.20         266.00         11           5.4427         7.4450         7.6441         266.20         266.00         11           5.44	$Pr_{0.2}Sm_{0.35}Sr_{0.45}MnO_3$	5.4533	5.4380	7.6786	219.03	219.03	16	1st order (AFM, FM)-PM transition
5.5038         7.7388         5.4746         226.00         226.00         1           5.4032         5.4859         2.30.00         226.00         18           5.4823         5.4859         2.30.00         230.00         14           5.4382         5.4839         7.6773         230.00         233.00         16           5.4382         5.439         7.6773         240.00         240.00         14           5.4318         5.4329         7.6759         241.20         241.20         241.00         16           5.4317         7.7602         5.5196         241.20         242.00         14         16           5.4317         7.7602         5.5190         256.00         242.00         14         14           5.4427         5.4427         7.6491         2.56.00         243.00         14         14           5.4427         5.4420         7.6491         2.66.20         265.00         14         14           5.4427         5.4420         7.6441         266.20         265.00         14         14           5.4304         7.7531         5.4510         266.20         265.00         14         14           5.4305	$Pr_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$	5.4293	7.6691	5.4552	222.78	246.39	23	2nd order FM-PM transition
5.5121         7.7508         5.4859         230.00         230.00         18           5.4322         5.4387         7.6773         230.01         230.01         16           5.4382         5.4380         7.6773         240.00         240.00         240.00         16           5.4382         7.6732         7.6702         2.5196         242.00         241.20         16           5.4817         7.7602         5.5196         242.00         241.20         11           5.4827         5.4847         7.6814         242.00         241.20         11           5.4827         5.469         7.6919         256.00         243.00         14           5.4427         7.4647         7.6810         258.20         265.00         14           5.4427         7.7511         5.6510         265.00         265.00         14           5.4427         7.7521         5.660         265.00         266.00         14           5.4427         7.7541         265.00         266.00         266.00         14           5.4427         7.7521         5.4696         268.00         266.20         266.00         14           5.4333         7.6729         <	${\rm La_{0.5}Sm_{0.2}Sr_{0.3}Mn_{0.85}Fe_{0.15}O_3}$	5.5038	7.7388	5.4746	226.00	226.00	1	2nd order FM-PM transition
5.4623         5.4387         7.6779         230.01         230.01         16           5.4328         5.4329         7.6732         230.01         230.01         14           5.4329         7.6732         241.20         240.00         240.00         16           5.4329         7.6732         241.20         242.00         240.00         16           5.4375         5.4647         7.6814         242.00         242.00         11           5.4375         5.4647         7.6814         243.00         242.00         11           5.4427         5.4649         7.6810         258.02         256.00         11           5.4427         5.4460         2.68.00         256.00         14           5.4427         5.4415         7.6800         258.00         268.00         16           5.4427         5.4414         266.00         266.00         266.00         11           5.4129         7.6291         245.00         268.00         268.00         11           5.4129         7.6292         268.00         268.00         268.00         11           5.4139         7.6291         245.00         268.00         268.00         11	$\mathrm{La_{0.6}Pr_{0.1}Ba_{0.3}MnO_3}$	5.5121	7.7508	5.4859	230.00	230.00	18	2nd order FM-PM transition
5.4382         5.4632         7.6826         233.00         14           5.4318         5.4399         7.6733         240.00         240.00         16           5.4316         5.4399         7.6733         240.00         240.00         16           5.4317         7.7602         5.5636         242.00         242.00         17           5.4317         7.7602         5.6814         243.00         243.00         14           5.4327         5.4669         7.6914         256.00         243.00         14           5.4327         5.4679         265.00         265.00         14           5.4317         7.7591         5.6519         265.00         265.00         14           5.4427         5.4679         266.00         266.00         266.00         14           5.4417         5.6411         266.20         266.00         266.00         17           5.4303         7.6229         268.00         268.00         268.00         17           5.4304         5.4528         26.00         26.20         26.20         26.20         26.20         26.20           5.4304         7.7224         24529         26.00         26.20	$Pr_{0.3}Sm_{0.25}Sr_{0.45}MnO_3$	5.4623	5.4387	7.6779	230.01	230.01	16	1st order (AFM, FM)-PM transition
5.4718         5.4399         7.6773         240.00         240.00         16           5.4825         5.4429         7.6533         240.00         240.00         12           5.4825         5.4429         7.6634         241.20         241.20         12           5.4825         5.4429         7.6814         243.00         243.00         14           5.4427         5.4669         7.6819         256.00         256.00         14           5.4427         5.4669         7.6814         243.00         256.00         14           5.4427         5.4669         7.6441         266.00         268.00         268.00         11           5.4427         5.4415         7.6441         266.00         268.00         268.00         11           5.4427         5.4416         268.00         268.00         268.00         11           5.4415         7.6441         266.00         246.39         11           5.4428         7.7229         5.4589         268.00         246.39         11           5.4439         7.6441         266.00         246.39         1         1           5.507         7.7403         5.4589         280.00         24	$Pr_{0.6}Ca_{0.1}Sr_{0.3}Mn_{0.95}Fe_{0.05}O_3$	5.4382	5.4632	7.6826	233.00	233.00	14	2nd order FM-PM transition
5.4825         5.4429         7.6503         241.20         241.20         12           5.4917         7.7602         5.5196         242.00         242.00         11           5.4377         5.4649         7.6814         243.00         242.00         14           5.4477         5.4669         7.6919         256.00         256.00         14           5.4427         5.4669         7.6919         256.00         256.00         14           5.4427         7.7591         5.5519         256.00         265.00         16           5.4437         7.7591         5.5619         266.20         265.00         11           5.4415         7.7541         5.5619         266.20         268.00         11           5.4019         7.7321         5.4698         268.14         266.00         11           5.4030         7.6729         5.4678         266.00         268.00         11           5.4303         7.6729         5.4578         268.14         266.11         266.20         268.14           5.4304         7.6731         5.4578         290.00         246.39         1         1           5.4306         7.6763         5.4484         <	$Pr_{0.4}Sm_{0.15}Sr_{0.45}MnO_3$	5.4718	5.4399	7.6773	240.00	240.00	16	1st order (AFM, FM)-PM transition
5.4917         7.7602         5.5196         242.00         242.00         11           5.4375         5.4647         7.6814         243.00         243.00         14           5.4427         5.4645         7.6814         256.00         256.00         14           5.4427         5.4415         7.6800         258.82         16           5.4427         5.4415         7.6800         258.82         16           5.4427         7.7591         5.5519         265.00         265.00         11           5.4015         7.7521         5.6620         266.20         266.20         11           5.4016         7.7421         5.6620         266.20         11           5.4026         5.6800         268.00         266.20         11           5.4036         7.6691         5.4568         286.00         12           5.4036         7.6793         2.68.00         268.14         268.14         268.14           5.5036         7.7403         5.4578         280.00         279.99         1           5.5047         5.4588         7.7263         292.24         292.23         3           5.4306         7.6705         5.4484         3	$Pr_{0.5}K_{0.05}Sr_{0.45}MnO_3$	5.4825	5.4429	7.6503	241.20	241.20	12	2nd order FM-PM transition
5.4375         5.4647         7.6814         243.00         243.00         14           5.4427         5.4669         7.6919         256.00         256.00         14           5.4427         5.4669         7.6919         256.00         265.00         16           5.4915         7.7511         5.5519         265.00         265.00         11           5.4916         7.7321         5.4696         268.00         266.20         11           5.5019         7.7321         5.4696         268.00         266.20         11           5.5036         7.7252         5.4678         280.00         246.39         4           5.5046         7.7262         5.4740         285.00         246.39         1           5.5027         7.7403         5.4740         285.00         284.99         1           5.4306         7.6703         5.4740         285.00         284.99         1           5.4306         7.6703         5.4484         300.80         300.80         23           5.4306         7.6703         5.4484         300.80         30.80         24           5.4306         7.6703         5.4484         300.80         30.80         2	$Nd_{0.67}Ba_{0.33}Mn_{0.98}Fe_{0.02}O_{3}\\$	5.4917	7.7602	5.5196	242.00	242.00	11	2nd order FM-PM transition
5.4427         5.4669         7.6919         256.00         256.00         14           5.4427         5.4415         7.680         258.82         16           5.4427         7.7321         5.5519         265.00         268.00           5.4015         7.7321         5.4666         268.00         266.00         11           5.4016         7.7321         5.4699         268.00         268.00         12           5.4030         7.6691         5.4599         268.14         268.14         268.14           5.4036         7.7629         268.00         268.14         268.14         25           5.4036         7.7629         2.4589         268.14         268.14         268.14         268.14           5.4036         7.6639         2.4678         285.00         246.39         4           5.4578         7.7463         292.24         287.99         1           5.4578         7.4676         285.00         300.80         300.80         3           5.4306         7.6705         5.4484         300.80         300.80         23         2           5.4306         7.6705         5.4484         300.80         30.869         2         <	$Pr_{0.6}Ca_{0.1}Sr_{0.3}MnO_3$	5.4375	5.4647	7.6814	243.00	243.00	14	2nd order FM-PM transition
5.4427         5.4415         7.6800         258.82         258.82         16           5.4915         7.7591         5.519         265.00         265.00         11           5.4915         7.7591         265.00         266.20         11           5.5019         7.7321         5.4996         268.00         268.00         12           5.4936         7.6729         268.14         266.20         12           5.4303         7.6729         5.4578         270.00         246.39         1           0s0         5.5036         7.7252         5.4678         280.00         246.39         1           0s         5.5036         7.7252         5.4678         280.00         246.39         1           0s         5.5036         7.7252         5.4678         280.00         246.39         1           0s         5.5047         5.4678         280.00         285.00         246.39         1           0s         5.5048         7.7252         5.4484         300.80         284.99         1           0s         7.6496         7.7484         300.80         300.80         23           5.4306         7.6892         5.4484         3	$Pr_{0.6}Ca_{0.1}Sr_{0.3}Mn_{0.925}Fe_{0.075}O_{3}\\$	5.4427	5.4669	7.6919	256.00	256.00	14	2nd order FM-PM transition
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Pr_{0.1}Sm_{0.45}Sr_{0.45}MnO_3$	5.4427	5.4415	7.6800	258.82	258.82	16	1st order (AFM, FM)-PM transition
5.4772       5.4420       7.6441       266.20       266.20       12         5.5019       7.7321       5.4696       268.00       268.00       12         5.4033       7.6729       5.4599       268.14       268.14       268.14         0s03       5.5037       7.7252       270.00       246.39       1         0s3       5.5037       7.7403       5.4740       285.00       284.99       1         0s       5.5037       7.7403       5.4740       285.00       284.99       1         0s       5.5027       7.7403       5.4740       285.01       284.99       1         0s       5.5027       7.7403       5.4740       285.00       284.99       1         0s       5.5027       7.7403       5.4749       285.21       282.23       3         5.5441       5.4661       7.734       292.24       292.23       3       3         5.4306       7.6675       5.4484       300.80       300.80       23       3         5.4306       7.6708       5.458       337.40       337.38       24         5.4460       7.6718       35.62       37.82       35.49       24	$\mathrm{Nd}_{0.67}\mathrm{Ba}_{0.33}\mathrm{MnO}_{3}$	5.4915	7.7591	5.5519	265.00	265.00	11	2nd order FM-PM transition
5.5019 7.7321 5.4696 268.00 268.00 1 1   5.4303 7.6729 5.4599 268.14 268.14 258.14 25   5.4303 7.6691 5.4552 270.00 246.39 4   5.4528 7.7252 5.4678 280.00 246.39 1   5.5641 5.4661 7.7374 285.00 248.99 1   5.4306 7.6705 5.4484 300.80 300.80   5.4306 7.6705 5.4484 300.80 300.80   5.4306 7.6705 5.4484 300.80 300.80   5.4306 7.6705 5.4484 300.80 300.80   5.4507 7.6705 3.4484 300.80 300.80   5.4507 7.6705 3.4484 300.80 300.80   5.4507 7.6705 3.484 300.80 300.80   5.4507 7.6705 3.484 300.80 300.80   5.4507 7.6708 3.4080 308.70 308.69   5.4508 5.4508 3.740 335.62 325.91   5.4509 7.6608 5.4508 337.40 337.81   5.4300 7.6679 5.4572 378.20 378.18   5.4300 7.6679 5.4572 405.02 405.85   5.4300 7.6679 6.9903 6.1761 239.44   5.4636 6.9903 6.1761 239.44   5.4630   5.4630    5.4630	$Pr_{0.5}Na_{0.05}Sr_{0.45}MnO_3$	5.4772	5.4420	7.6441	266.20	266.20	12	2nd order FM-PM transition
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\mathrm{La_{0.5}Sm_{0.2}Sr_{0.3}MnO_3}$	5.5019	7.7321	5.4696	268.00	268.00	1	2nd order FM-PM transition
5.4293         7.6691         5.4552         270.00         246.39         4           0.69         5.5036         7.7252         5.4678         280.00         279.99         1           (03         5.5027         7.7403         5.4740         285.00         284.99         1           5.5027         7.7403         5.4740         285.00         284.99         1           5.4578         7.7403         5.4744         280.24         292.23         3           5.4578         7.7403         5.4784         300.80         300.80         300.80         3           5.4306         7.6705         5.4484         300.80         300.80         300.80         23           5.4306         7.6705         5.4484         300.80         300.80         300.80         23           5.4307         7.6708         5.4496         337.40         37.38         24           5.4420         7.6718         352.20         378.20         378.20         24           5.4299         7.6696         5.4572         378.20         378.20         24           5.4300         7.6679         5.4572         406.00         405.85         405.85         4      <	$Pr_{0.7}Ca_{0.3}Mn_{0.98}Co_{0.02}O_3$	5.4303	7.6729	5.4599	268.14	268.14	25	2nd order FM-PM transition
0.60         5.5036         7.7252         5.4678         280.00         279.99         1           0.3         5.5027         7.7403         5.4740         285.00         284.99         1           5.5027         7.7403         5.4740         285.00         284.99         1           5.5041         5.4588         7.7263         292.24         292.23         3           5.5441         5.4661         7.7374         293.21         293.20         3           5.4306         7.6705         5.4484         300.80         300.80         23           5.4328         7.6892         5.4195         308.70         308.69         23           5.4328         7.6892         5.4195         308.70         308.69         23           5.4329         7.6743         5.4648         337.40         337.38         24           5.4321         7.6748         35.220         355.61         355.61         3           5.4460         5.4481         7.7113         355.62         378.20         378.18         24           5.4314         7.6714         5.4591         378.20         378.18         24           5.4300         7.6679         5.4572	$Pr_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$	5.4293	7.6691	5.4552	270.00	246.39	4	1st order FM-PM transition
O3         5.5027         7.7403         5.4740         285.00         284.99         1           5.4578         5.458         7.7263         292.24         292.23         3           5.5641         5.4661         7.7374         293.21         293.20         3           5.4306         7.6705         5.4484         300.80         300.80         23           5.4306         7.6705         5.4484         300.80         308.69         23           5.4328         7.6892         5.4195         308.70         308.69         23           5.4320         7.6708         5.4648         337.40         337.38         24           5.4321         7.6743         5.4648         337.40         352.19         24           5.4460         5.4481         7.7113         355.62         352.19         24           5.4295         7.6696         5.4572         378.20         378.20         24           5.4314         7.6711         5.4591         378.20         378.18         25           5.4300         7.6679         5.4572         406.00         405.85         4           5.4636         6.9903         6.1761         239.44         239.	${\rm La_{0.5}Sm_{0.2}Sr_{0.3}Mn_{0.95}Fe_{0.05}O_3}$	5.5036	7.7252	5.4678	280.00	279.99	1	2nd order FM-PM transition
5.4578       5.4584       7.7263       292.24       292.23       3         5.5641       5.4661       7.7374       293.21       293.20       3         5.4306       7.6705       5.4484       300.80       300.80       23         5.4306       7.6705       5.4484       300.80       300.80       25         5.4328       7.6892       5.4195       308.70       308.69       23         5.4507       5.4525       7.7165       325.98       325.97       3         5.4321       7.6743       5.4648       337.40       337.38       24         5.4295       7.6708       5.4508       352.20       352.19       24         5.4460       5.4481       7.7113       355.62       355.61       3         5.4299       7.6696       5.4572       378.20       378.18       25         5.4314       7.6711       5.4591       378.20       378.18       25         5.4300       7.6679       5.4572       406.00       405.85       4         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       -239.44 <td< td=""><td><math>{ m La_{0.5}Sm_{0.2}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3}</math></td><td>5.5027</td><td>7.7403</td><td>5.4740</td><td>285.00</td><td>284.99</td><td>1</td><td>2nd order FM-PM transition</td></td<>	${ m La_{0.5}Sm_{0.2}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3}$	5.5027	7.7403	5.4740	285.00	284.99	1	2nd order FM-PM transition
5.5641         5.4661         7.7374         293.21         293.20         3           5.4306         7.6705         5.4484         300.80         300.80         23           5.4306         7.6705         5.4484         300.80         300.80         25           5.4328         7.6892         5.4195         308.70         308.69         23           5.4507         5.4525         7.7165         325.98         325.97         3           5.4321         7.6743         5.4648         337.40         357.38         24           5.4295         7.6708         5.4508         352.20         352.19         24           5.4290         7.6696         5.4572         378.20         378.20         24           5.4314         7.6711         5.4591         378.20         378.18         25           5.4300         7.6679         5.4572         406.00         405.85         4           5.4300         7.6679         5.4572         406.00         405.85         4           5.4300         7.6679         5.4572         406.00         405.85         4           5.4636         7.6679         5.4572         406.00         405.85	$Pr_{0.8}Na_{0.1}K_{0.1}MnO_3$	5.4578	5.4588	7.7263	292.24	292.23	3	2nd order FM-PM transition
5.4306         7.6705         5.4484         300.80         300.80         23           5.4306         7.6705         5.4484         300.80         300.80         25           5.4328         7.6892         5.4195         308.70         308.69         23           5.4507         5.4525         7.7165         325.98         325.97         3           5.4321         7.6743         5.4648         337.40         337.38         24           5.4295         7.6708         5.450         355.20         355.19         24           5.4290         7.6696         5.4572         378.20         378.20         24           5.4314         7.6711         5.4591         378.20         378.18         25           5.4300         7.6679         5.4572         406.00         405.85         4           5.4300         7.6679         5.4572         406.00         405.85         4           5.4636         6.9903         6.1761         239.44	$\mathrm{Pr}_{0.8}\mathrm{Na}_{0.05}\mathrm{K}_{0.15}\mathrm{MnO}_{3}$	5.5641	5.4661	7.7374	293.21	293.20	3	2nd order FM-PM transition
5.4306         7.6705         5.4484         300.80         300.80         25           5.4328         7.6892         5.4195         308.70         308.69         23           5.4507         5.4525         7.7165         325.98         325.97         3           5.4321         7.6743         5.4648         337.40         357.38         24           5.4295         7.6708         5.450         352.20         352.19         24           5.4460         5.4481         7.7113         355.62         378.20         378.20         24           5.4304         7.6696         5.4572         378.20         378.18         25           5.4314         7.6711         5.4591         378.20         378.18         25           5.4300         7.6679         5.4572         406.00         405.85         4           5.4300         7.6679         5.4572         406.00         405.85         4           5.4636         6.9903         6.1761         239.44         239.44         -	$Pr_{0.7}Ca_{0.3}Mn_{0.9}Co_{0.1}O_3$	5.4306	7.6705	5.4484	300.80	300.80	23	2nd order FM-PM transition
5.4328         7.6892         5.4195         308.70         308.69         23           5.4507         5.4525         7.7165         325.98         325.97         3           5.4321         7.6743         5.4648         337.40         352.97         3           5.4295         7.6708         5.4508         352.20         352.19         24           5.4460         5.4481         7.7113         355.62         355.61         3           5.4299         7.6696         5.4572         378.20         378.20         24           5.4314         7.6711         5.4591         378.20         378.18         25           5.4300         7.6679         5.4572         406.00         405.85         4           5.4300         7.6679         5.4572         406.00         405.85         4           5.4636         6.9903         6.1761         239.44	$Pr_{0.7}Ca_{0.3}Mn_{0.9}Co_{0.1}O_3$	5.4306	7.6705	5.4484	300.80	300.80	25	2nd order FM-PM transition
5.4507       5.4525       7.7165       325.98       325.97       3         5.4321       7.6743       5.4648       337.40       337.38       24         5.4295       7.6708       5.481       7.7113       355.62       355.19       24         5.4299       7.6696       5.4572       378.20       378.20       24         5.4314       7.6711       5.4591       378.20       378.18       25         5.4300       7.6679       5.4572       405.72       405.85       24         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$Pr_{0.7}Ca_{0.3}Mn_{0.9}Ni_{0.1}O_3$	5.4328	7.6892	5.4195	308.70	308.69	23	2nd order FM-PM transition
5.4321       7.6743       5.4648       337.40       337.38       24         5.4295       7.6708       5.4508       352.20       352.19       24         5.4460       5.4481       7.7113       355.62       355.61       3         5.4299       7.6696       5.4572       378.20       378.20       24         5.4314       7.6711       5.4591       378.20       378.18       25         5.4300       7.6679       5.4572       406.00       405.85       4         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$Pr_{0.8}Na_{0.15}K_{0.05}MnO_3$	5.4507	5.4525	7.7165	325.98	325.97	3	1st order FM-PM transition
5.4295         7.6708         5.4508         352.20         352.19         24           5.4460         5.4481         7.7113         355.62         355.61         3           5.4299         7.6696         5.4572         378.20         378.20         24           5.4314         7.6711         5.4591         378.20         378.18         25           5.4300         7.6679         5.4572         406.00         405.85         24           5.4636         6.9903         6.1761         239.44         239.44         —	$Pr_{0.7}Ca_{0.3}Mn_{0.95}Fe_{0.05}O_3$	5.4321	7.6743	5.4648	337.40	337.38	24	2nd order FM-PM transition
5.4460       5.4481       7.7113       355.62       355.61       3         5.4299       7.6696       5.4572       378.20       378.20       24         5.4314       7.6711       5.4591       378.20       378.18       25         5.4300       7.6679       5.4572       405.72       405.85       24         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$Pr_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$	5.4295	7.6708	5.4508	352.20	352.19	24	2nd order FM-PM transition
5.4299       7.6696       5.4572       378.20       378.20       24         5.4314       7.6711       5.4591       378.20       378.18       25         5.4300       7.6679       5.4572       405.72       405.85       24         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$\mathrm{Pr}_{0.8}\mathrm{Na}_{0.2}\mathrm{MnO}_{3}$	5.4460	5.4481	7.7113	355.62	355.61	3	1st order (AFM, FM)-PM transition
5.4314       7.6711       5.4591       378.20       378.18       25         5.4300       7.6679       5.4572       405.72       405.85       24         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$Pr_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$	5.4299	7.6696	5.4572	378.20	378.20	24	2nd order FM-PM transition
5.4300       7.6679       5.4572       405.72       405.85       24         5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$Pr_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_{3}$	5.4314	7.6711	5.4591	378.20	378.18	25	2nd order FM-PM transition
5.4300       7.6679       5.4572       406.00       405.85       4         5.4636       6.9903       6.1761       239.44       239.44       —	$Pr_{0.7}Ca_{0.3}Mn_{0.95}Cr_{0.05}O_3$	5.4300	7.6679	5.4572	405.72	405.85	24	2nd order FM-PM transition
5.4636 6.9903 6.1761 239.44	$Pr_{0.7}Ca_{0.3}Mn_{0.95}Cr_{0.05}O_3$	5.4300	7.6679	5.4572	406.00	405.85	4	2nd order FM-PM transition
	Mean	5.4636	6.9903	6.1761	239.44	239.44	1	I

Fable 1 (Contd.)

Sample	a (Å)	<i>b</i> (Å)	c (Å)	Experimental relative cooling power (J $kg^{-1}$ )	Predicted relative cooling power (J kg $^{-1}$ )	Reference	Reference Magnetic property
Median	5.4520	7.6710	5.4743	249.50	246.39	I	I
Standard deviation	0.0340	1.0638	1.0452	98.66	98.52	1	I
Minimum	5.4293	5.4380	5.4195	3.67	3.70	I	1
Maximum	5.5641	7.8002	7.7374	406.00	405.85	1	I
Correlation coefficient	-30.47%	-15.67%	14.69%	1	99.87%	I	1
with relative cooling power							

"a (Å)," "b (Å)," and "c (Å)" are lattice parameters. "Predicted relative cooling power (J kg<sup>-1</sup>)" shows the result from the current work, meaning predicted values based on the Gaussian process egression. "Experimental relative cooling power (J kg<sup>-1</sup>)" and "Predicted relative cooling power (J kg<sup>-1</sup>)" are visualized in Fig. 2. " $\square$ " in sample names stands for "vacancy." "FM" means ferromagnetism," "AFM" means "anti-ferromagnetism," and "PM" means "paramagnetism egression. "Experimental relative cooling power (J kg

of modifications from the cubic structure by the deformation of the MnO<sub>6</sub> octahedron arising from the Jahn–Teller effect and/or changes in the connective pattern of the MnO<sub>6</sub> octahedra in the perovskite structure. <sup>26,27</sup> Values of  $T_{\rm C}$ , magnetic entropy changes  $\Delta S_{\rm m}$ , adiabatic temperature changes  $\Delta T_{\rm ad}$ , and the resultant RCP are strongly dependent on the doping mechanisms and thus lattice distortions.

Qualitative analysis on the effect of dopant types and levels on RCP of lanthanum manganites has been conducted through experiments, mainly by varying synthesis methods (solid-state reaction, wet chemistry, sol–gel, *etc.*), morphologies (particle size, shape, *etc.*), crystalline states, and final forms (powder, pellet, film, *etc.*). <sup>1,3,4,11-14,16-18,23-25</sup> Quantitative analysis through thermodynamics models and first-principle models has been utilized to aid the understanding of magnetothermal responses of these materials and facilitate the searching of new candidates for MR devices. <sup>2,5,7,15</sup> However, these models require a significant amount of data inputs, such as variables for equations of state, exchange coupling energies, and magnetic moments of magnetocaloric materials, which can only be obtained by extensive measurements.

In this work, the Gaussian process regression (GPR) model is developed to elucidate the statistical relationship between RCP and lattice parameters of orthorhombic lanthanum manganites. The model generalizes well in the presence of only a few descriptive features, where intelligent algorithms are able to learn and recognize the patterns. This modeling approach demonstrates a high degree of accuracy and stability, contributing to efficient and low-cost estimations of RCP and understandings of which based on lattice parameters. As one of the computational intelligence techniques, the GPR model has already been utilized in other materials systems to predict significant physical parameters in different fields of applications.31-44 On one hand, the model can serve as a guideline for searching for doped-manganites with a large RCP value by screening the lattice parameters. On the other hand, the model can be used as part of machine learning to aid the understanding of the magnetic phase transformation in various types of doped-manganites.

The remaining of this work is organized as follows. Section 2 proposes the GPR model. Section 3 describes the data and computational methodology. Section 4 presents and discusses results, and Section 5 concludes.

# 2 Proposed methodology

#### 2.1 Brief description of Gaussian process regression

GPRs are nonparametric kernel-based probabilistic models. Consider a training dataset,  $\{(x_i,y_i); i=1,2,...,n\}$  where  $x_i \in \mathbb{R}^d$  and  $y_i \in \mathbb{R}$ , from an unknown distribution. A trained GPR predicts values of the response variable  $y^{\text{new}}$  given an input matrix  $x^{\text{new}}$ .

Recall a linear regression model,  $y = x^T \beta + \varepsilon$ , where  $\varepsilon \sim N(0, \sigma^2)$ . A GPR aims at explaining y by introducing latent variables,  $l(x_i)$  where i = 1, 2, ..., n, from a Gaussian process such that the joint distribution of  $l(x_i)$ 's is Gaussian, and explicit basis functions, b. The covariance function of  $l(x_i)$ 's captures the

smoothness of y and basis functions project x into a feature space of dimension p.

A GP is defined by the mean and covariance. Let m(x) = E(l(x)) be the mean function and k(x,x') = Cov[l(x),l(x')] the covariance function, and consider now the GPR model,  $y = \frac{1}{2} \sum_{i=1}^{n} \frac{$ 

 $b(x)^T \beta + l(x)$ , where  $l(x) \sim \text{GP}(0, k(x, x'))$  and  $b(x) \in \mathbb{R}^p$ . k(x, x') is often parameterized by the hyperparameter,  $\theta$ , and thus might be written as  $k(x, x' | \theta)$ . In general, different algorithms estimate  $\beta$ ,  $\sigma^2$ , and  $\theta$  for model training and would allow specifications of b and k, as well as initial values for parameters.

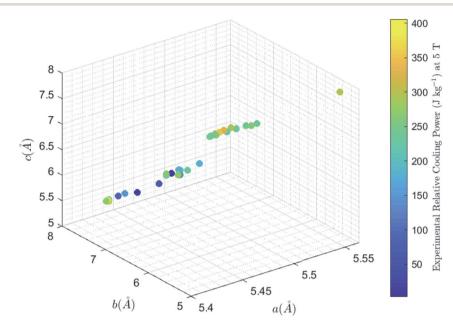


Fig. 1 Magnetic cooling power and lattice parameters, a (Å), b (Å), and c (Å).

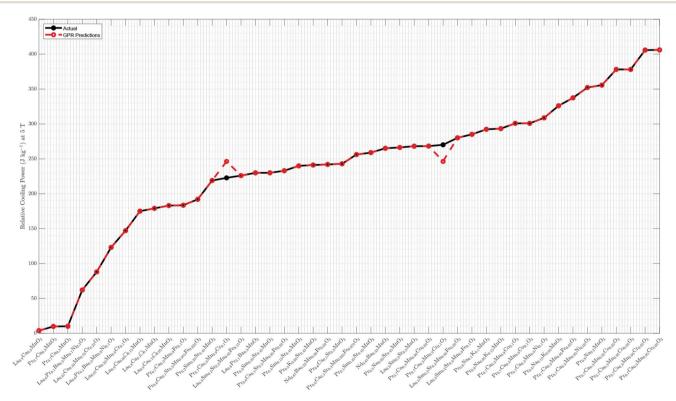


Fig. 2 Experimental vs. predicted relative cooling power. The GPR model is built using the whole sample with the Matern 5/2 kernel, constant basis function, and standardized lattice parameters. It has a log-likelihood of -813.7988,  $\hat{\beta}$  of 233.9604,  $\hat{\sigma}$  of 0.9866,  $\hat{\sigma}_l$  of 0.0053, and  $\hat{\sigma}_f$  of 89.8778. Detailed numerical predictions are listed in Table 1 (Column 6). " $\square$ " in sample names stands for "vacancy".

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The current study explores four kernel functions, namely exponential, squared exponential, Matern 5/2, and rational quadratic, whose specifications are listed in eqn (1)-(4), respectively, where  $\sigma_1$  is the characteristic length scale defining how far apart x's can be for y's to become uncorrelated,  $\sigma_f$  is the signal standard deviation,  $r = \sqrt{(x_i - x_j)^T(x_i - x_j)}$ , and  $\alpha$  is a positive-valued scale-mixture parameter. Note that  $\sigma_{\rm l}$  and  $\sigma_{\rm f}$ should be positive. This could be enforced through  $\theta$  such that  $\theta_1 = \log \sigma_1$  and  $\theta_2 = \log \sigma_f$ .

$$k(x_i, x_j | \theta) = \sigma_f^2 \exp\left(-\frac{r}{\sigma_1}\right)$$
 (1)

$$k(x_i, x_j | \theta) = \sigma_f^2 \exp \left[ -\frac{1}{2} \frac{(x_i - x_j)^T (x_i - x_j)}{\sigma_l^2} \right]$$
 (2)

$$k(x_i, x_j | \theta) = \sigma_f^2 \left( 1 + \frac{\sqrt{5}r}{\sigma_1} + \frac{5r^2}{3\sigma_1^2} \right) \exp\left( -\frac{\sqrt{5}r}{\sigma_1} \right)$$
(3)

$$k(x_i, x_j | \theta) = \sigma_f^2 \left( 1 + \frac{r^2}{2\alpha\sigma_1^2} \right)^{-\alpha}$$
 (4)

Similarly, three basis functions are investigated here, namely constant, linear, and pure quadratic, whose specifications are listed in eqn (5)-(7), respectively, where  $B = (b(x_1), b(x_2), ...,$ 

$$b(x_n)^T$$
,  $X = (x_1, x_2, ..., x_n)^T$ , and  $X^2 = \begin{pmatrix} x_{11}^2 & x_{12}^2 & \cdots & x_{1d}^2 \\ x_{21}^2 & x_{22}^2 & \cdots & x_{2d}^2 \\ \vdots & \vdots & \vdots & \vdots \\ x_{n1}^2 & x_{n2}^2 & \cdots & x_{nd}^2 \end{pmatrix}$ .

$$B = I_{n \times 1} \tag{5}$$

$$B = [1, X] \tag{6}$$

$$B = [1, X, X^2] \tag{7}$$

To estimate the GPR model, a Bayesian optimization algorithm is utilized. With a Gaussian process model of f(x), the algorithm evaluates  $y_i = f(x_i)$  for  $N_s$  points  $x_i$  taken at random within the variable bounds, where  $N_s$  points stand for the number of initial evaluation points and 4 is used. If there are evaluation errors, it takes more random points until  $N_s$ successful evaluations are arrived-at. The algorithm then repeats the following two steps: (1) updating the Gaussian process model of f(x) to obtain a posterior distribution over functions  $Q(f|x_i,y_i \text{ for } i=1,\ldots,n)$ ; (2) finding the new point xthat maximizes the acquisition function a(x). It stops after reaching 30 iterations. The acquisition function, a(x), evaluates the goodness of a point, x, based on the posterior distribution function, O. This work employs the lower-confidence-bound (LCB) acquisition function, which looks at the curve G two standard deviations,  $\sigma_O$ , below the posterior mean,  $\mu_O$ , at each point:  $G(x) = \mu_O(x) - 2\sigma_O(x)$ . Therefore, G(x) is the  $2\sigma_O$  lower confidence envelope of the objective function model. The algorithm then maximizes the negative of G: LCB =  $2\sigma_O(x)$  –  $\mu_O(x)$ . The optimization is carried out on  $\sigma$ , the noise standard deviation.  $\theta$  and  $\beta$  are estimated by maximizing the log likelihood function.

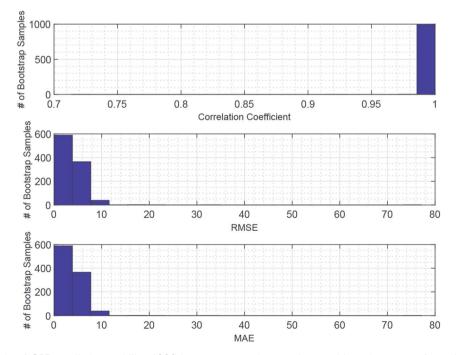


Fig. 3 Bootstrap analysis of GPR prediction stability. 1000 bootstrap samples are drawn with replacements from the whole sample. Each bootstrap sample is used to train the GPR based on the Matern 5/2 kernel and constant basis function with lattice parameters standardized, and obtain the associate model performance. The histograms show distributions of the CC, RMSE, and MAE over the 1000 bootstrap samples, whose averages are 99.87%, 2.7915, and 0.9800, respectively

Table 2 GPR prediction sensitivities to kernel and basis function choices<sup>a</sup>

Kernel	Basis function	CC	RMSE	RMSE/sample mean	MAE	MAE/sample mean
Matern 5/2	Constant	99.87%	5.0339	2.10%	1.0923	0.46%
Rational quadratic	Constant	99.87%	5.0458	2.11%	1.3362	0.56%
Squared exponential	Constant	99.87%	5.0345	2.10%	1.1389	0.48%
Exponential	Constant	99.87%	5.1248	2.14%	1.7993	0.75%
Matern52	Linear	99.87%	5.0339	2.10%	1.0947	0.46%
Matern52	Pure quadratic	99.87%	5.0339	2.10%	1.0940	0.46%

<sup>&</sup>lt;sup>a</sup> The final GPR model is based on the Matern 5/2 kernel and constant basis function.

#### 2.2 Performance evaluation

Performance of the proposed GPR models is evaluated using the root mean square error (RMSE), mean absolute error (MAE), and correlation coefficient (CC) in eqn (8), (9), and (10) respectively, where n is the number of data points,  $T_i^{\rm exp}$  and  $T_i^{\rm est}$  are the i-th (i=1,2,...,n) experimental and estimated magnetic cooling power, and  $\overline{T^{\rm est}}$  and  $\overline{T^{\rm est}}$  are their averages.

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( T_i^{\text{exp}} - T_i^{\text{est}} \right)^2}$$
 (8)

$$MAE = \frac{1}{n} \sum_{i=1}^{n} |T_i^{exp} - T_i^{est}|$$
 (9)

$$CC = \frac{\sum_{i=1}^{n} (T_i^{\text{exp}} - \overline{T^{\text{exp}}}) (T_i^{\text{est}} - \overline{T^{\text{est}}})}{\sqrt{\sum_{i=1}^{n} (T_i^{\text{exp}} - \overline{T^{\text{exp}}})^2 \sum_{i=1}^{n} (T_i^{\text{est}} - \overline{T^{\text{est}}})^2}}$$
(10)

# 3 Empirical study

#### 3.1 Description of dataset

The experimental data used, shown in Table 1 (Columns 1–5), are obtained from ref. 1, 3, 4, 11–14, 16–18 and 23–25, most of which have been modeled through the support vector machine regression model. The dataset covers a wide range of doped lanthanum manganites in the form of bulk polycrystalline, single crystal, powders, and sintered pellets, by different synthesis routes including the solid-state reaction, wet-mix processing, and sol–gel processing. RCP values are calculated from  $\Delta S_{\rm m}$  and the full width at half maximum (FWHM) of the  $\Delta S_{\rm m}$  vs. T curve under  $\Delta (\mu_0 H)$  of 5 T. Data visualization in Fig. 1 reveals nonlinear relationships, which are modeled through the GPR.

#### 3.2 Computational methodology

MATLAB is utilized for computations and simulations in this work. All observations are used to train the final GPR model given the relative small sample size. The stability of the GPR approach is confirmed by bootstrap analysis.

## 4 Result and discussion

## 4.1 Comparison with previous study

The final GPR model is detailed in Fig. 2, whose performance is compared with that based on the SVM regression in ref. 19.† Switching from the SVM to GPR, the CC increases from 85.07% to 99.87%, the RMSE decreases from 50.5315 to 5.0339, and the MAE decreases from 26.3802 to 1.0923. The GPR model thus provides more accurate relative cooling power predictions than the SVM regression. The result in Fig. 2 shows good alignment between GPR predicted and experimental data.

#### 4.2 Prediction stability

Given the small sample size (see Table 1) used, the prediction stability of the GPR is assessed through bootstrap analysis in Fig. 3, which shows that the modeling approach maintains high CCs, low RMSEs, and low MAEs over the bootstrap samples. This result suggests that the GPR might be generalized for magnetic cooling power modeling of manganite materials based on larger samples.

#### 4.3 Prediction sensitivity

Table 2 shows that GPR predictions are not so sensitive to choices of kernels or basis functions. Because predictions based on different kernel-basis function pairs are so close and nearly visually indistinguishable, they are not plotted for comparisons. However, it is worth noting that estimated model parameters are different across these kernel-basis function pairs.

# 5 Conclusions

The Gaussian process regression (GPR) model is developed to predict relative cooling power of manganite materials based on lattice parameters. The high correlation coefficient between the predicted and experimental magnetic cooling power, the low prediction root mean square error and mean absolute error, and stable model performance suggest the usefulness of the GPR for

<sup>†</sup> The comparison is not 100% one-to-one because nine additional observations are used in ref. 19. The data are split into the training and validation sub-samples in ref. 19, where the former has 43 observations and the latter 10. We compare model performance of the GPR with that of the SVM regression<sup>19</sup> by focusing on their 43 training observations.

modeling and understanding the relationship between lattice parameters and relative cooling power. This modeling approach is straightforward and simple and requires less parameters as compared to thermodynamics models and first-principle models. It can be used as part of computational intelligence approaches for new magnetocaloric materials searches.

# Conflicts of interest

There are no conflicts to declare.

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