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Magnetotransport, thermophysical and magnetocaloric properties of manganite $La_{0.8}Ag_{0.1}MnO_3$ in magnetic fields up to 8 T

© A.G. Gamzatov[1,2], A.T. Kadyrbardeev[1], G.M. Aliev[1], R.R. Abdurazakov[1], M.N. Markelova[3], A.B. Batalov[1], A.M. Aliev[1]

[1] Amirkhanov Institute of Physics, Dagestan Federal Research Center, Russian Academy of Sciences, Makhachkala, Dagestan Republic, Russia
[2] Dagestan State University, Makhachkala, Dagestan Republic, Russia
[3] Lomonosov Moscow State University, Moscow, Russia

E-mail: gamzatov_adler@mail.ru

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The electrical resistance, heat capacity, thermal conductivity, thermal conductivity and magnetocaloric effect of the polycrystalline sample $La_{0.8}Ag_{0.1}MnO_3$ were measured in the temperature range 77−350 K and in magnetic fields up to 8 T. It is shown that electrical resistance in the paramagnetic phase can be explained within the framework of the concept of small-radius polarons with an activation energy of $E_P = 119$ meV, and the behavior of electrical resistance in the low-temperature ferromagnetic phase suggests the existence of several scattering mechanisms. The observed large magnitude of the magnetoresistive effect at low temperatures is explained by the intergranular tunneling of conduction electrons. An anomalous abrupt change in the lattice heat capacity during the ferromagnetic-paramagnetic phase transition was detected. The increase in thermal conductivity and thermal conductivity observed below the Curie temperature T_C is associated with the scattering of phonons by local Jahn-Teller distortions, which weaken during the transition to the ferromagnetic phase. The magnetocaloric effect in a magnetic field of 8 T reaches a value of Delta $\Delta T_{ad} = 4$ K, and the value of the efficiency of magnetic cooling in the same field is 261.6 J/kg. Keywords: manganites, electrical resistance, heat capacity, thermal conductivity, thermal conductivity, magnetocaloric effect.

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1. Introduction

The continuing interest in perovskite manganites is due to the fact that they have a complex phase diagram and are model objects for studying the properties of strongly correlated electronic systems. The presence of colossal magnetoresistance (CMR) [1] and magnetocaloric effect (MCE) [2] in them suggests their use in modern innovative technologies. Therefore, a comprehensive study of the material properties is an urgent task and can enable to better understand the nature of the effects observed in them.

Manganites doped with monovalent ions (Na, K, Ag) have a number of significant differences from the well-studied manganites $Ln_{1-x}A_xMnO_3$, where A — divalent metal (Ca, Sr, ...). When the parent composition $LaMnO_3$ is doped with monovalent Ag^+ ions, to maintain the charge balance, it is required that for each introduced monovalent Ag^+ ion, two Mn^{3+} ions pass to the Mn^{4+} state, which means a narrowing of the $T-x$ phase diagram along the x axis and high values of the T_C Curie temperature at a low doping level ($x < 0.2$) [3,4]. Silver-doped manganites $La_{1-x}Ag_xMnO_3$ are distinguished by a high sensitivity of their physical properties to a magnetic field; CMR and MCE effects appear at room temperature [2–7]. Previously, it was shown that non-stoichiometric compositions $La_{1-x}Ag_yMnO_3$ ($y < x$) have a number of advantages, the observed effects in them are pronounced [4,8].

This report provides the results of a complex experimental study of the properties of a polycrystalline $La_{0.8}Ag_{0.1}MnO_3$ sample in the temperature range T from 80 to 350 K and in magnetic fields up to 8 T. In particular, electrical resistance ρ, magnetoresistance $\Delta\rho/\rho_0$, heat capacity C_p, temperature conductivity η, thermal conductivity κ, magnetocaloric effect were studied.

The studied sample was obtained using the method of chemical homogenization according to a technology similar to that described in [5], but differs from the previously studied samples in terms of synthesis. The resulting sample had a single-phase ceramic microstructure with an average grain size $\sim 1.5\,\mu$m [9] and a rhombohedral crystal structure $R\bar{3}c$. The sample density is $d = 4.23$ g/cm^3, which roughly corresponds to $\sim 72\%$ of the theoretical value.

Electrical resistance was measured by the standard four-probe method, heat capacity and temperature con-

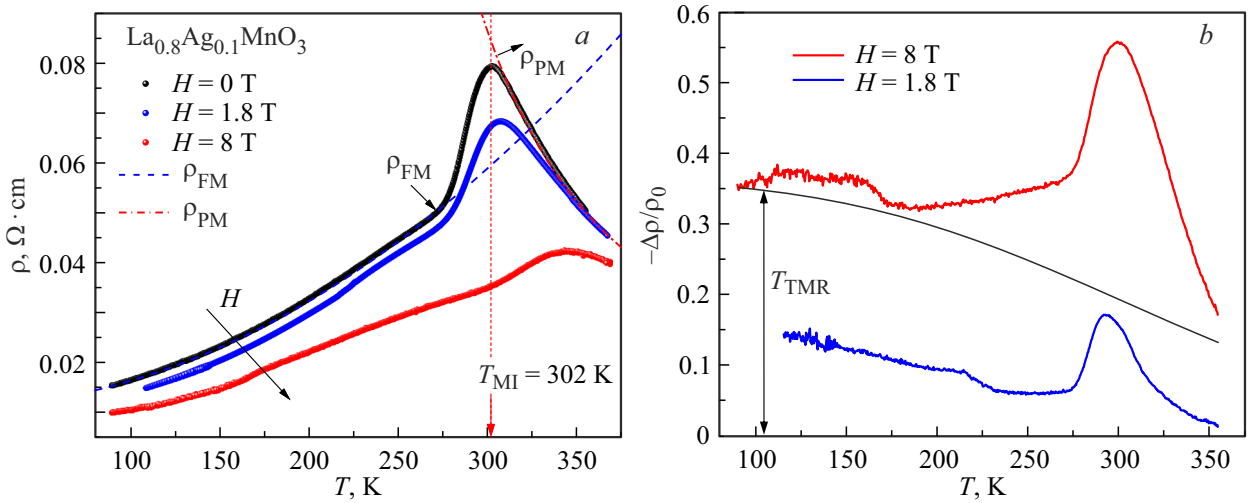

Figure 1. *a* — temperature dependence of electrical resistance for $La_{0.8}Ag_{0.1}MnO_3$. *b* — magnetoresistive effect in fields 1.8 and 8 T, the dashed line corresponds to the tunneling contribution to the magnetoresistive effect.

ductivity were measured by modulation calorimetry (AC-calorimetry). The thermal conductivity was determined as their product: $\kappa = C_p \eta d$ (d — sample density). Direct measurements of the MCE were carried out by the method of magnetic field modulation [10]. Chromel-constantan thermocouples (0.05 mm in diameter) were used as temperature sensors.

2. Results and discussion

Figure 1, *a* shows the temperature dependences of the electrical resistance of the $La_{0.8}Ag_{0.1}MnO_3$ sample in magnetic fields of 0, 1.8 and 8 T, while Figure 1, *b* demonstrates the magnetoresistive effect. The temperature dependence of the electrical resistance has a bell shape characteristic of manganites, associated with the transition of the sample from the dielectric (paramagnetic) to the metallic (ferromagnetic) phase at $T_{MI} = 302$ K. In magnetic field, the electrical resistance is suppressed over the entire temperature range, thus demonstrating the CMR effect.

In the high-temperature dielectric phase, the $\rho(T)$ dependence has a semiconductor character, can be interpreted on the basis of the concept of small-radius polarons, and is well approximated by the thermal activation law of the form

$$\rho(T) = DT \exp(E_p/k_B T), \qquad (1)$$

where E_p is activation energy of the polaron, D is temperature-independent coefficient, k_B is Boltzmann constant. Approximation of experimental data using expression (1) allows us to estimate the values of E_p and D: $D = 2.9 \cdot 10^{-6}\ \Omega \cdot$ cm/K, $E_p = 119$ meV. The coefficient D is related to the concentration of charge carriers n in the paramagnetic phase, in this case, polarons, by the expression [11]: $D = 2k_B/3ne^2\alpha\nu$, where α is the length of the polaron jump, which approximately coincides with the parameters of the crystal lattice, ν is frequency of optical phonons, e is electron charge. Using the values α and ν characteristic of manganites: $\alpha = 5.4$ Å, $\nu = 4 \cdot 10^{13}$ Hz and the experimentally estimated value of $D = 2.9 \cdot 10^{-6}\ \Omega \cdot$ cm/K, we obtain the concentration of charge carriers (polarons) $n = 0.98 \cdot 10^{21}$ cm^{-3}, the value of which is in good agreement with the previously obtained data [4].

The behavior of the electrical resistance in the low-temperature ferromagnetic phase can be described using an expression that includes several scattering mechanisms

$$\rho(T) = \rho_0 + AT^2 + BT^{4.5}, \qquad (2)$$

where ρ_0 is residual electrical resistance, term AT^2 is attributed to electron-electron scattering, $BT^{4.5}$ — to scattering of current carriers by magnons. In fact, it would not be entirely correct to confidently assert that this is the case. The contribution from interelectron collisions is usually observed at very low temperatures and is relatively small. The coefficient A for transition metals is by 4–6 orders less than in our case ($A = 5.32 \cdot 10^{-6}\ \Omega \cdot$ cm/K^2). The contribution $BT^{4.5}$ attributed to the electron-magnon interaction can just as well be related to the scattering of electrons by phonons at low temperatures ($\rho_{e-ph} \propto T^5$). Most likely, we are dealing with a superposition of several scattering mechanisms (electron-electron, electron-magnon, electron-phonon), which ultimately lead to the observed form of the $\rho(T)$ dependence in a certain temperature range (77–280 K).

In the immediate vicinity of the phase transition, the dependence $\rho(T)$ is not described by expressions (1) and (2): when the sample passes into the low-temperature ferromagnetic phase, a sharp increase in conductivity is observed, which cannot be explained within the framework of the considered models. However, if we assume that the metal-dielectric phase transition in this system is a

percolation phase transition, the observed behavior of the electrical resistance can be explained in terms of percolation theory [3,12].

The degree of influence of the magnetic field on the electrical resistance is determined by the ratio $-\Delta\rho/\rho = ((\rho_H - \rho_0)/\rho_0) \cdot 100\%$, which determines magnitude of the magnetoresistive effect. As can be seen in Fig. 1, *b*, the maximum values of the magnetoresistive effect are equal to $\sim 17\%$ (at temperature of 292 K) and $\sim 53\%$ (at 299 K) in magnetic fields 1.8 and 8 T, respectively. A distinctive feature of the observed magnetoresistance effect in the sample under study is that it manifests itself not only near T_C, but also at low temperatures (Fig. 1, *b*). Usually, in single-crystal manganites, the CMR effect is observed near the phase transition temperature, while far from T_C it tends to zero on the right and left. The observed behavior can be explained by the ceramic nature of the sample under study. The magnetoresistive effect in $La_{0.8}Ag_{0.1}MnO_3$ is determined by two independent mechanisms: the double exchange mechanism near T_C and the intergranular spin-polarized tunneling of charge carriers, the contribution of which increases with decreasing temperature [13,14].

Figure 2 shows the temperature dependence of the heat capacity in various magnetic fields (0, 1.8, 8 T). One can see characteristic abnormalities near T_C associated with the transition from the ferromagnetic phase to the paramagnetic phase at $T_C = 286$ K. In a magnetic field, the abnormality is suppressed and the maximum shifts towards higher temperatures. In addition to the indicated characteristic abnormalities near T_C, there is another abnormality in the behavior of $C_p(T)$, which consists in the fact that the heat capacity immediately before and after the phase transition both in zero field and in fields of 1.8 and 8 T is not approximated by a continuous line without any features. In other words, an abnormal jump-like change in the lattice heat capacity by the $\Delta C_p \approx 20$ J/mol · K value is observed. In other compounds of the $La_{1-x}Ag_xMnO_3$ system, such abnormalities have not been previously observed [6,15]. It is possible that the abnormality also has a magnetic nature, which is associated with the magnetic heterogeneity of the sample, due to which additional energy is required to destroy the remaining „frozen-in" magnetization, which requires higher magnetic fields (more than 8 T). We exclude structural transformations near T_C. In any case, this issue requires further research.

Figure 3, *a* shows the temperature dependence of the temperature conductivity $\eta(T)$. Note that the temperature conductivity characterizes the rate of change in the temperature of the material in non-stationary thermal processes and is equal to the ratio of the thermal conductivity coefficient to the product of the specific heat capacity of the material and the density: $\eta = \kappa/C_p d$. As can be seen in Fig. 3, *a*, $\eta(T)$ decreases with increasing temperature, and near T_C it sharply changes its slope, passing into a state that is almost no temperature dependent. The magnetic field smoothes the $\eta(T)$ curve and shifts the bending temperature towards higher temperatures.

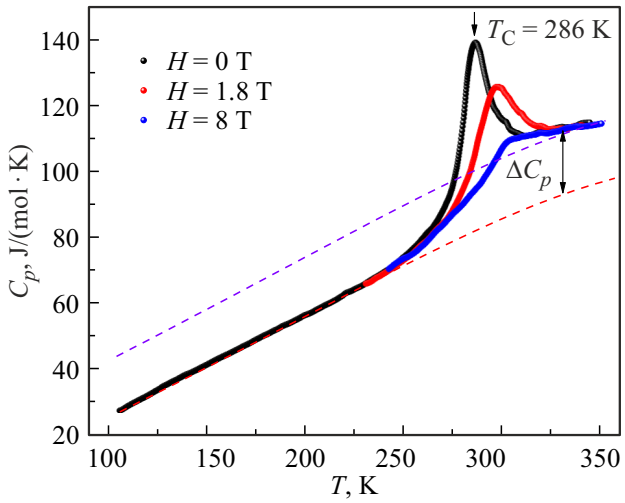

Figure 2. Temperature dependence of the heat capacity measured in the heating mode for a $La_{0.8}Ag_{0.1}MnO_3$ sample in magnetic fields 0, 1.8 and 8 T.

As is known, in materials with purely phonon thermal conductivity, in fact, the dependence $\eta(T)$ is the dependence of the phonon mean free path length on temperature: $l_{ph}(T) = 3\eta(T)/\upsilon_s$, where l_{ph} is phonon mean free path length, υ_s is sound speed. The results of our measurements of $\rho(T)$ and $\rho(T)$ and the Wiedemann–Franz law $\kappa_e = LT/\rho$ (L — Lorentz number) allow us to say that we are dealing with just such a case, where $\kappa_{ph} \gg \kappa_e$. Taking the characteristic values of the sound speed for manganites $\upsilon_s = 5 \cdot 10^5$ m/s [16], we estimated $l_{ph}(T)$, the result of the estimation is shown in the inset in Fig. 3, *a*. It can be seen that the $l_{ph}(T)$ pattern repeats $\eta(T)$, and its absolute value does not exceed several lattice cell parameters. Physically, this means that the distortions on which phonons scatter must be of the same order of magnitude as l_{ph}. Local distortions of the crystal lattice caused by the Jahn–Teller effect are considered as such distortions.

Figure 3, *b* shows the temperature dependences of thermal conductivity at $H = 0.1.8$ and 8 T. The temperature variation and relatively low values κ are characteristic of most manganites [17,18]. In the high-temperature paramagnetic phase ($T > T_C$), the thermal conductivity remains constant, independent of T. This corresponds to the experimental data on $C_p(T)$ and $l_{ph}(T)$, which do not depend on T for $T > T_C$, and to the phonon gas thermal conductivity theory, according to which $\kappa = (1/3)C_v l_{ph}\upsilon_s$. With a decrease in temperature at the transition to the ferromagnetic phase, the thermal conductivity experiences an abrupt increase: $(\kappa_{FM} - \kappa_{PM})/\kappa_{PM} = 0.44$, where κ_{FM}, κ_{PM} are thermal conductivities in the ferromagnetic and paramagnetic phases, which are associated with a decrease in the rate of phonon scattering on local distortions of MnO_6 octahedra caused by the Jahn–Teller effect. Upon transition to the ferromagnetic phase, distortions are removed, which

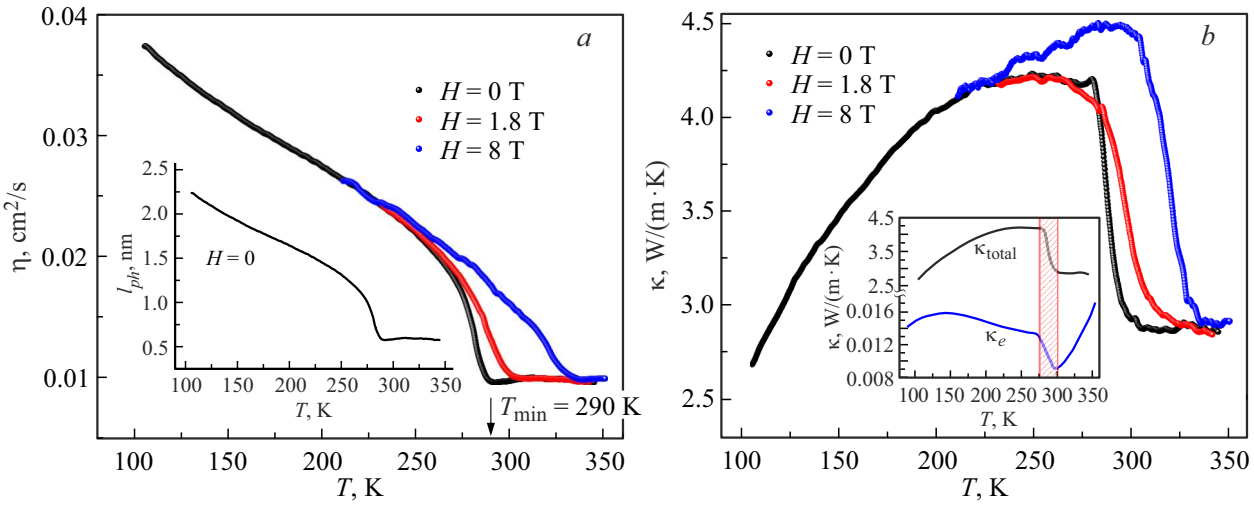

Figure 3. *a* — temperature dependence of temperature conductivity. The inset shows dependence graph $l_{ph} = f(T)$. *b* — temperature dependence of temperature conductivity. The inset shows the total electron thermal conductivity and temperature conductivity calculated on the basis of the Wiedemann-Franz ratio, the temperature interval where abnormalities are observed is marked with a line.

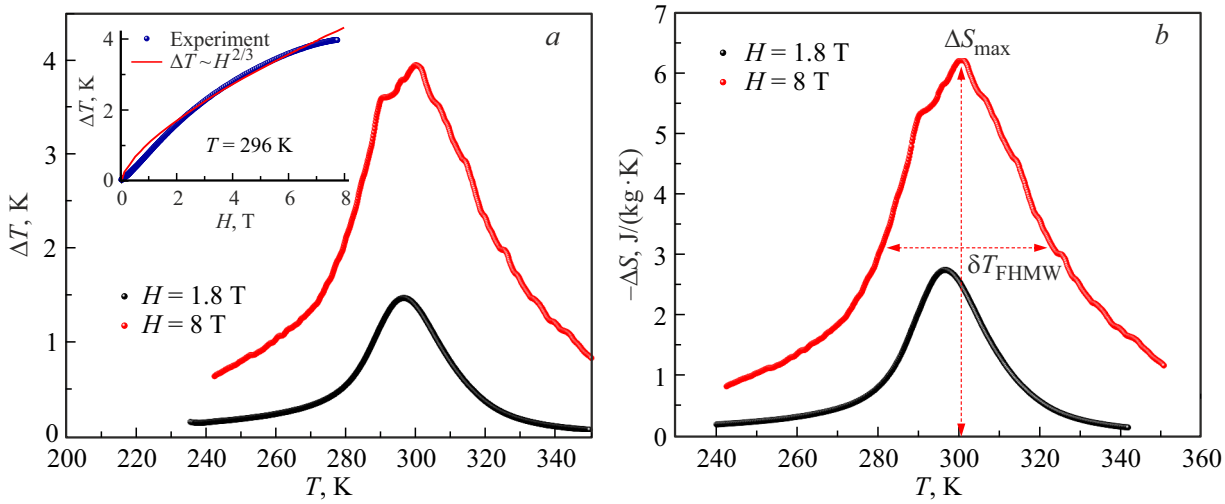

Figure 4. *a* — temperature dependence of MCE for $La_{0.8}Ag_{0.1}MnO_3$ in fields 1.8 and 8 T. The inset shows the dependence $\Delta T(H)$ at $T = 296$ K. *b* — temperature dependence of entropy change for $La_{0.8}Ag_{0.1}MnO_3$ in fields 1.8 and 8 T.

causes a sharp increase in thermal conductivity. The magnetic field, while maintaining ferromagnetic ordering up to higher temperatures, suppresses Jahn-Teller distortions, which leads to an increase in thermal conductivity below T_C.

Figure 4, *a* shows the results of direct measurements of the temperature dependence of the MCE in fields 1.8 and 8 T. The maximum MCE value is $\Delta T = 1.47$ K and $\Delta T = 4$ K in fields 1.8 and 8 T respectively. These values are comparable with data for other $La_{1-x}Ag_xMnO_3$ [8] compounds, as well as manganites of other compositions jcite2. The inset in Fig. 4, *a* shows the dependence of MCE on the magnetic field at $T = 296$ K. As shown in [19], the field dependence of MCE near T_C in materials with second-order phase transitions has a power-law form: $\Delta S \propto H^n$, where $n = 1$ for $T \ll T_C$, $n = 2$ at $T \gg T_C$ and $n = 0.75$ near T_C. In [20] it is shown that the dependence $\Delta T_{max} = f(H)$ for the $La_{1-x}K_xMnO_3$ in the range of magnetic fields 1.8–8 T is described by the expression $\Delta T \propto H^{0.64}$. This behavior is in good agreement with the predictions of the mean field theory, which gives the dependence $\Delta S \propto H^{2/3}$ [21]. The $\Delta T(H)$ dependence for the $La_{0.8}Ag_{0.1}MnO_3$ sample shown in the inset in Fig. 4, *a* also agrees well with the predictions of the mean field theory (see the thin red line in the inset) and shows that a second-order phase transition occurs in this sample.

Figure 4, *b* shows the temperature dependences of the change in the magnetic entropy ΔS_M obtained using the relation $-\Delta S_M = \Delta T_{ad} C_P(T, H)/T$ [22], where ΔT_{ad} is experimental data of direct measurements, $C_P(T, H)$ is temperature dependence of heat capacity in a magnetic

field. The maximum entropy change is $6.21\,\mathrm{J/(kg\cdot K)}$ in a magnetic field 8 T. Estimates of the magnetic cooling efficiency $R_C = \int_{T_1}^{T_2} \Delta S_M(T,H)dT$ in a magnetic field 8 T show, that the quantity $R_C = 261/6\,\mathrm{J/kg}$. Although it is not a record among manganites [2,23,24] the value obtained for the efficiency of magnetic cooling in a magnetic field 8 T for the $La_{0.8}Ag_{0.1}MnO_3$ sample makes this composition attractive for magnetic cooling technology, since the maxima of the effect occur at room temperatures.

3. Conclusion

Thus, comprehensive studies of the magnetotransport, thermophysical, and magnetocaloric properties of a polycrystalline $La_{0.8}Ag_{0.1}MnO_3$ sample are carried out in the temperature range 77−350 K and in magnetic fields up to 8 T. It is shown that in the paramagnetic region the behavior of the electrical resistance fits within the framework of the concept of small-radius polarons with activation energy $E_p = 119$ meV. The electrical resistance in the ferromagnetic phase is well described by an expression that includes several scattering mechanisms. The concentration of charge carriers in the paramagnetic dielectric phase is estimated. The observed large magnitude of the magnetoresistive effect at low temperatures is explained by intergranular electron tunneling.

Abnormal behavior of the heat capacity is found, which consists in a jump-like change in the lattice part of the heat capacity during the phase transition from the ferromagnetic phase to the paramagnetic one by the value of $\Delta C_p = 20\,\mathrm{J/(mol\cdot K)}$. The abnormalities in thermal conductivity and temperature conductivity observed at $T = T_C$ are associated with a decrease in the rate of phonon scattering on Jahn–Teller distortions in the ferromagnetic phase. It is shown that in $La_{0.8}Ag_{0.1}MnO_3$ manganite a large MCE value is observed ($\Delta T = 4$ K at $\Delta H = 8$ T) near room temperatures, which makes this material a possible candidate as a working fluid for magnetic cooling devices.

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Conflict of interest

The authors declare that they have no conflict of interest.

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