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Magnetocaloric effect in powder of GdTbDyHoEr high-entropy alloy

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The paper presents the results of studying the structural, magnetic and magnetocaloric properties of the powder of GdTbDyHoEr high-entropy alloy obtained by ball milling a rapidly quenched nanocrystalline ribbon of this alloy. When the temperature and external magnetic field change, a magnetic phase transition between a helical antiferromagnet and ferromagnet occurs in the powder. The change in the magnetic entropy ΔS_M was determined based on the Maxwell relation from the magnetic isotherms data. The maximum value of ΔS_M is observed at a temperature of 178 K and for a magnetic field change amplitude of 9 T it is 12.1 $\mathrm{Jkg^{-1} \cdot K^{-1}}$.

Keywords: high entropy alloy, crystal structure, magnetic phase transitions, magnetocaloric effect, refrigerant capacity.

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1. Introduction

The magnetic cooling technology is currently seen as a promising alternative to steam and gas technology, which offers prospects to reduce power consumption, level of noise and mechanical oscillations, to eliminate use of ozone-depleting gases. Magnetocaloric effect (MCE), which describes the reversible change of magnetic material temperature when exposed to variable magnetic field, is the basis of the magnetic cooling [1]. Active research is in progress to find the corresponding magnetocaloric materials that may maintain high values of adiabatic change of temperature, change of the magnetic part of entropy and high cooling capacity [2]. These parameters to a large extent are determined by the value of the magnetic moment of the material, the type of magnetic phase transition (first- or second-order phase transition), implemented in the cooling agent material, and features of such transition [2]. From the point of view of the magnetic moment value, the most promising are the heavy rare earth elements still [3].

A critical factor is the mechanical strength of the working material in a magnetic refrigerator, therefore, recently, while searching for the new effective magnetocaloric materials, more and more attention is paid to high-entropy alloys (HEA), having improved mechanical properties [1,4]. Quite recently it was shown that five and more metal components taken as equal mole fractions, could form a single-phase crystalline alloy. And atoms of various types are placed in the lattice sites randomly. HEA is a disordered substitutional solid solution, with no long-range order for each type of atoms. Disordered position of all atoms in the lattice sites causes higher configuration entropy of such phase, hence the name of such alloys [5]. Studies of magnetocaloric properties of HEA based on heavy rare earth elements demonstrated promising nature of these materials for magnetic cooling [6]. Apart from the high value of entropy magnetic part variation inherent in heavy rare earth elements, this is also caused by the presence of two subsequent magnetic phase transitions in some of them as temperature decreases: paramagnetic — helicoidal antiferromagnetic and helicoidal antiferromagnetic — ferromagnetic [7–9]. In the presence of the external magnetic field as temperature changes, a sequence of magnetic transitions is implemented in these elements between some diverse magnetic phases [10]. The effect of this is a wide maximum on the temperature dependence of entropy magnetic part variation and increased cooling capacity [11]. Currently attempts are being made to improve efficiency of MCE in high-entropy alloys based on heavy rare earth elements by variation of their elemental composition [11–13].

Efficiency of the magnetic refrigerator is determined not only by the material of its working material, but also the shape that it is represented in. The powder has additional advantages both in terms of heat transfer efficiency and the design of specific devices. However, data differ regarding magnetocaloric properties of the material in powder state. In particular, the example of gadolinium shows that powder may be both the same in properties to volume specimens [14], or be substantially inferior thereto [15].

This paper is dedicated to the comparative study of the features of crystalline structure, magnetic and magnetocaloric properties of the powder of high-entropy alloy GdTbDyHoEr.

2. Study methodology

Powder GdTbDyHoEr was produced by grinding rapid-quenched nanocrystalline tape of this alloy in the en-

vironment of ethyl alcohol for 10 hours. The ratio of masses of steel balls and ground tape was 66 : 1. Tape GdTbDyHoEr was formed by rapid quenching by pouring alloy GdTbDyHoEr produced by induction melting onto the surface of a rotary copper disc. Alloy components were taken in equal mole fractions. The linear rotation speed of the quenching surface of the disc was 40 m/s. The produced tape had width of 1 mm and thickness of 30 μm.

The powder structure was studied using X-ray diffraction analysis (diffractometer PHILIPS X'PERT PRO (radiation Cu-K_α)) and transmission electron microscopy (microscope JEM-2100). Magnetic measurements were made on measuring complex PPMS DynaCool 9T.

3. Results and discussion

Figure 1 shows the images of powder particles obtained using optical microscope (a) and transmission electron microscopy (b), and Fourier-processing of high resolution image (c). One may see that these are particles of irregular shape, with a wide scatter in size from dozens of microns to dozens of nanometers. The largest particles making the main volume of the powder have the shape of scales or flakes, which seems to be due to the fact that the source material for grinding was a tape. Particles of different size may be combined into conglomerates.

The X-ray diffraction analysis showed that the particles of GdTbDyHoEr powder have hexagonal structure (space group $P63/mmc$). Besides, the best match of the experiment and calculation was for the parameters of lattice $a = 3.6029(10)$ Å and $c = 5.66901(46)$ Å (Figure 2, insert), which correlates well with both calculated and experimental data given for the similar alloy in paper [11]. Diffractograms also contain low intensity lines not related to the main phase of GdTbDyHoEr. As a rule, they are related to a solid solution of rare earth elements with symmetry $Fm-3m$ [16]. Probable presence of such phase in the studied powders was taken into account in X-ray diffraction analysis (Figure 2, insert). Two lines of the undetermined phase (vertical lines on the insert of Figure 2) may be the result of formation of rare earth oxides or hydrides, taking into account the method of powder preparation [13]. Besides, the relative content of the phase of high-entropy alloy GdTbDyHoEr is approximately 95%.

Note the intensive line (002), which most probably means that the preferable orientation of crystallites is the one where the basis plane is parallel to the surface of particles (scales). Using this line, the average size of crystallites was identified using Scherrer formula, it was 26 ± 3 nm. The estimates showed that the content of admixtures will not exceed 5 wt.%.

Figure 3 shows temperature dependences of GdTbDyHoEr powder magnetization $M(T)$, measured in the field $\mu_0 H = 0.01$ T using the method ZFC-FC (cooling in the zero field or cooling in the magnetic field of the specified value). The appearance of the FC curve

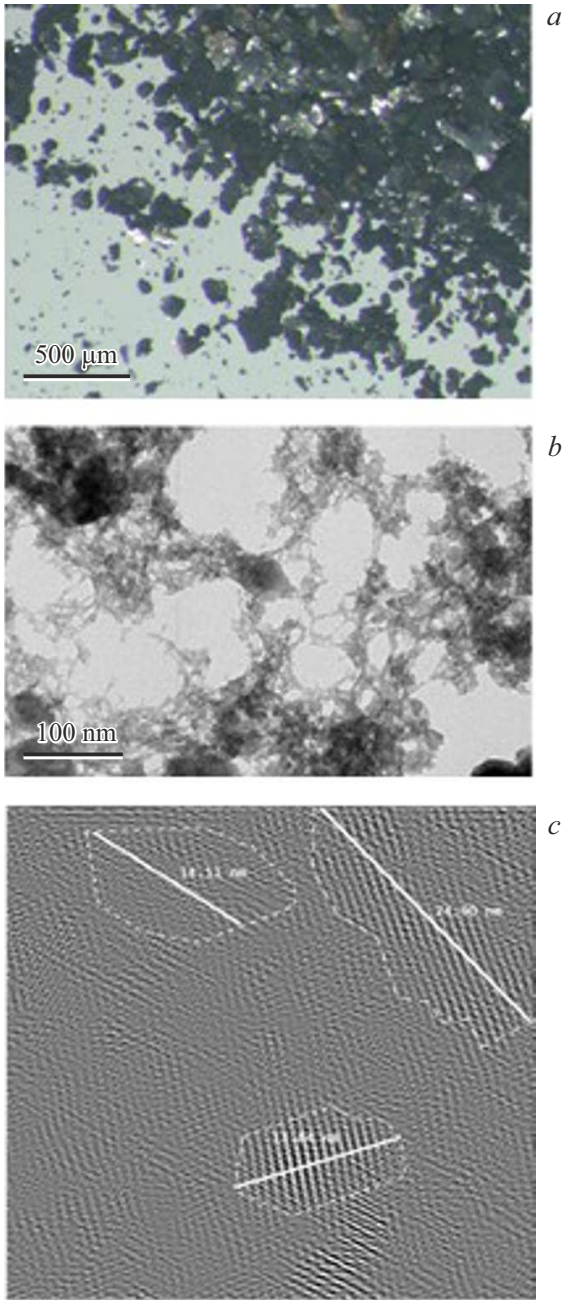

Figure 1. Images of GdTbDyHoEr powder particles obtained using optical microscope (a) and transmission electron microscopy (b), Fourier-processing of high resolution image (c).

reminds the behavior of the similar dependence $M(T)$ for Tb, Dy, Er and Ho, in which the two subsequent magnetic phase transitions are observed as temperature drops: transition from paramagnetic state (PM) to helicoidal antiferromagnetic state (HAFM) and spin-reorientation transition from HAFM state to ferromagnetic state (FM) [7,17]. The first transition relates to second-order phase transition, and temperature $T_N = 178$ K, at which dependence $M(T)$ demonstrates local maximum (Figure 3), is close to Neel temperature for dysprosium

$T_N = 179$ K [7,9], and values T_N for volume specimens of GdTbDyHoEr alloy [6,11]. Fast growth of magnetization at $T_N < 150$ K is the consequence of phase transition HAFM-FM [7,17]. Temperature hysteresis in the range of $70 < T < 150$ K confirms that this transition is related to first-order phase transition.

It is well-known that the external magnetic field influences the features of these magnetic phase transitions. It was shown on single crystal specimens of heavy rare earth elements that with orientation of the external magnetic field in the basis plane of the crystal, the temperature of phase transition HAFM-FM is shifted towards the region of higher temperatures, and of PM-HAFM transition — towards the region of low temperatures. At a certain critical field value the HAFM state will not be implemented, and the specimen, as the temperature drops, immediately changes from paramagnetic state to ferromagnetic one [7,17]. For the studied GdTbDyHoEr powder the value of such critical field was approximately equal to 1.6 T, as follows from Figure 4, which shows dependences $M(T)$, measured as the specimen is cooled in the presence of magnetic field that varies in value.

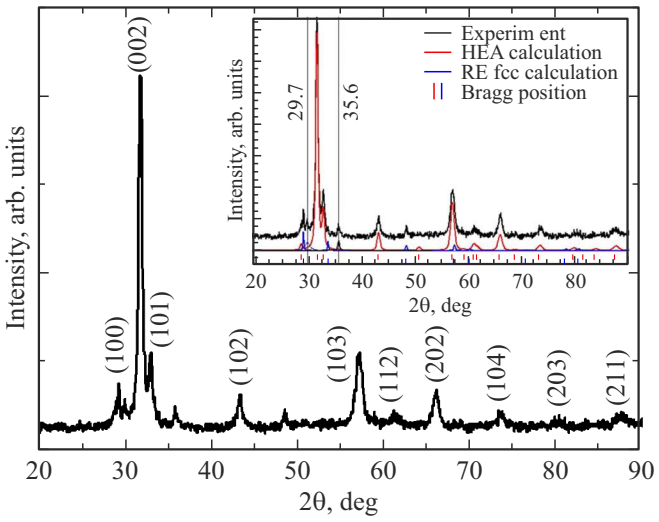

Figure 2. Diffractogram of GdTbDyHoEr powder. The insert shows the results of processing of an experimental diffractogram with account of phases of high-entropy alloy GdTbDyHoEr (HEA calculation) and solid solution of rare earth elements with symmetry $Fm{-}3m$ (RE fcc calculation); the vertical lines specify the lines corresponding to the undetermined phase.

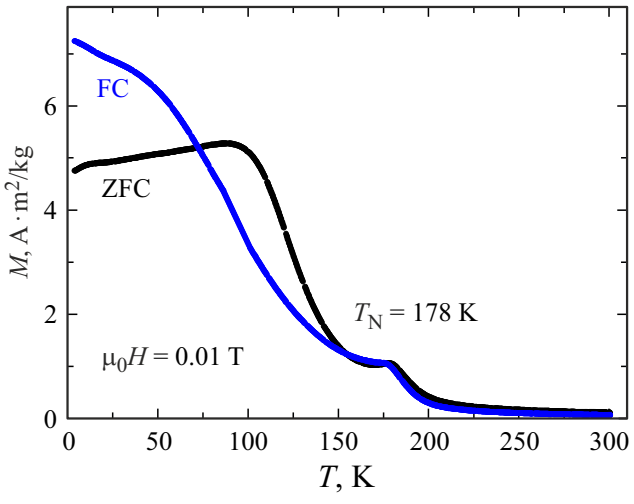

Figure 3. Temperature dependences of GdTbDyHoEr powder magnetization measured using method ZFC-FC at $\mu_0 H = 0.01$ T.

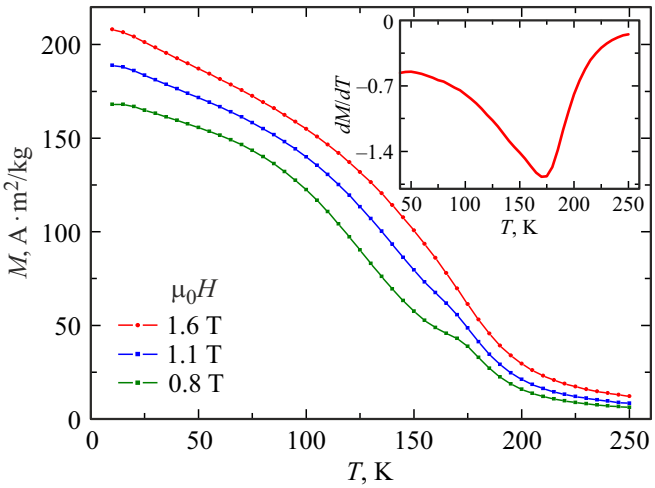

Figure 4. Temperature dependences of GdTbDyHoEr powder magnetization, measured during specimen cooling in presence of magnetic field that varies in value. The insert shows the temperature dependence of derivative dM/dT for $\mu_0 H = 1.6$ T.

Presence of metamagnetic phase transition HAFM-FM, induced by the external magnetic field, is confirmed by features on the magnetization curves measured at different temperatures. Figure 5 shows certain dependences $M(H)$. In the temperature range approximately from 120 to 170 K on the magnetization curves the linear section in small fields changes with a faster increase of magnetization M in large fields. Local maxima on dependences $M(T)$ (Figure 3) and bends on dependences $M(H)$ (Figure 5) for GdTbDyHoEr powder are less pronounced compared to what is observed on the corresponding dependences for single-crystal samples of heavy rare earth elements [7,17]. The value of the critical field, where HAFM-structure is damaged, depends on orientation of the magnetic field relative to crystallographic axes [7]. Therefore, the polycrystalline nature of the studied GdTbDyHoEr powder particles provides for flatness of bends on dependences $M(H)$. Besides, contrary to the pure rare-earth elements, random distribution of magnetic rare-earth atoms in the lattice sites of the high-entropy alloy causes complex magnetism in these disordered solid solutions. The mechanism of indirect exchange at the expense of Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction may produce various magnetic states [12], which provokes a succession of phase transitions that is indistinct by temperature and value of magnetic field between a row of various magnetic phases [10,18].

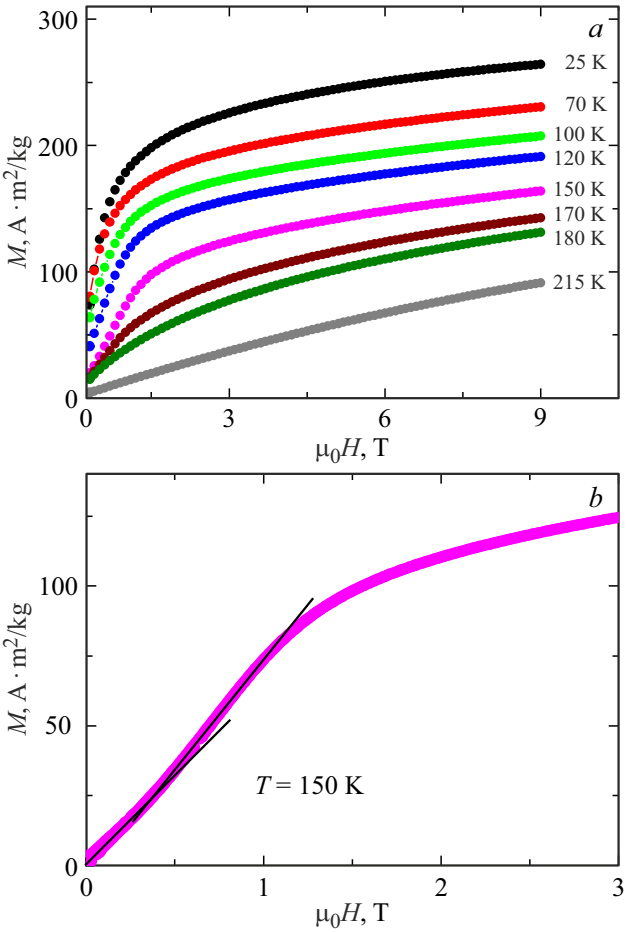

Figure 5. Curves of GdTbDyHoEr powder magnetization measured at different temperatures (a). More detailed view of a part of magnetization curve measured at $T = 150$ K (b).

Using magnetic isotherms, some of which are shown in Figure 5, a, based on the Maxwell relation, the change in the magnetic part of entropy was determined ΔS_M:

$$\Delta S_M = -\int_{H_2}^{H_1} \left(\frac{\partial M}{\partial T}\right)_H dH, \qquad (1)$$

where H — magnetic field, M — magnetization, T — temperature. Figure 6 presents temperature dependences $-\Delta S_M(T)$ of GdTbDyHoEr powder for various amplitudes of variation for the external field $\Delta\mu_0 H$.

One may see that at $\Delta\mu_0 H < 3$ T curves $-\Delta S_M(T)$ show a local minimum at $T \sim 165$ K. Similar nature of dependences was observed for rare earth elements, in particular, for Dy and Tm [7]. The peak near T_N is related to the fact that heat is released as a result of growing degree of magnetic order when exposed to external magnetic field in a paraprocess and under reduction of magnetic subsystem entropy, which in its turn causes growing entropy of the crystalline lattice. At lower temperatures the external fields both promotes increased degree of magnetic order and damage of antiferromagnetic structure, which is accompanied with heat absorption. In the temperature range from T_N to 165 K the effect of the damaging action of the field prevails, which results in lower value $-\Delta S_M(T)$. As the temperature reduces further, the increase in the degree of the order as a result of the damaging antiferromagnetic structure being exposed to the field becomes prevalent, and $-\Delta S_M(T)$ increases again. At $\Delta\mu_0 H \geq 3$ T the field suppresses formation of HAFM phase, therefore, as the temperature drops, phase transition PM-FM is implemented, bypassing the HAFM phase, and dependence $-\Delta S_M(T)$ acquires the typical form for such phase transition with a single maximum. Also note that for GdTbDyHoEr powder near the minimum of around 165 K the dependence $-\Delta S_M(T)$ will not change the sign, as it was observed for the volume specimens of GdTbDyHoEr alloy at $\Delta\mu_0 H \leq 2$ T in the narrow temperature range (negative MCE) [6].

Another significant feature of the magnetocaloric material is cooling capacity (RC), showing the quantity of heat transferred when cooling 1 kg of material per one thermodynamic cycle with a certain change of magnetic field [19,20]. Value RC is calculated in process of integration as the area under curve $-\Delta S_M(T)$. Besides, the limits of integration are the temperatures on the half of the peak height:

$$RC = \int_{T_1}^{T_2} |\Delta S_M(T)|\, dT, \qquad (2)$$

where T_1 and T_2 — temperatures corresponding to the value $-\Delta S_M(T)$ on the half of the peak height. Field dependences RC and $-\Delta S_M^{\max}$ are shown in Figure 7.

Paper [6] provides data for $-\Delta S_M^{\max}$ ($8.6\,\mathrm{J kg^{-1} \cdot K^{-1}}$) and cooling capacity RC ($627\,\mathrm{J kg^{-1}}$) at $\Delta\mu_0 H = 5$ T for the volume specimen of GdTbDyHoEr alloy. The value $-\Delta S_M^{\max}$ ($6.9\,\mathrm{J kg^{-1} \cdot K^{-1}}$) received for the studied GdTbDyHoEr powder is quite inferior to the parameter of the volume specimen, but by cooling capacity value RC ($600\,\mathrm{J kg^{-1}}$)

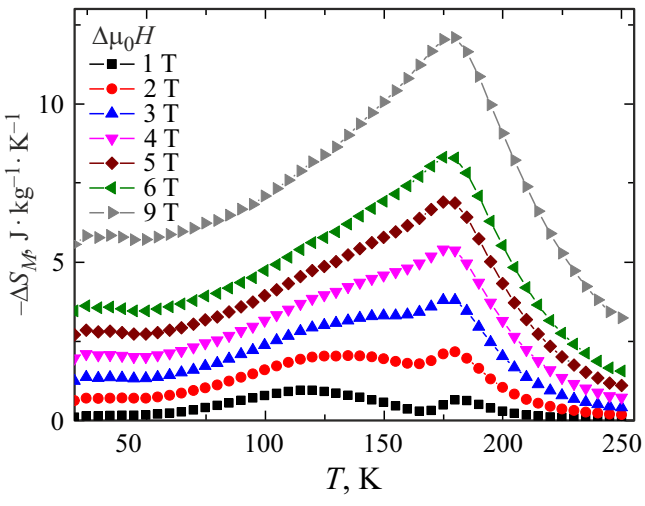

Figure 6. Temperature dependence of variation of GdTbDyHoEr powder entropy magnetic part.

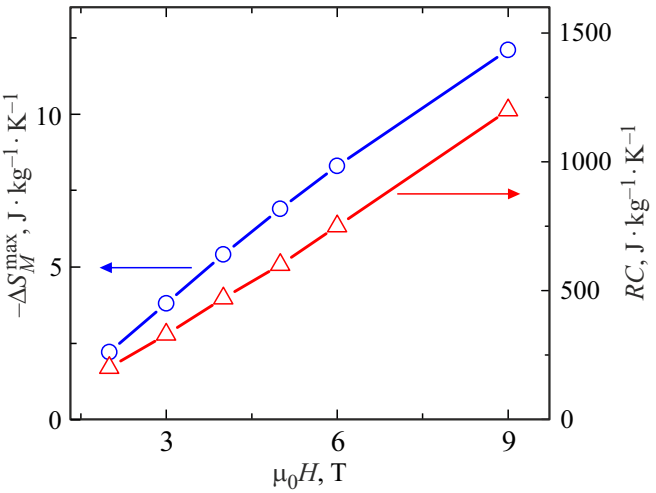

Figure 7. Field dependences of variation of magnetic part of entropy $-\Delta S_M^{\max}$ and cooling capacity RC of GdTbDyHoEr powder.

the powder is similar to the volume specimen. Magnetic systems based on state-of-the-art permanent magnets create fields up to 2 T [20]. Therefore, from the point of view of practical applications, the values of parameters are important that characterize the magnetocaloric material at $\Delta\mu_0 H \leq 2$ T. Therefore, for Gd granulated powder, value $-\Delta S_M^{\max} = 5\,\mathrm{J kg^{-1} \cdot K^{-1}}$ was obtained at $\Delta\mu_0 H = 2$ T [14], which is double of the similar value for GdTbDyHoEr powder (Figure 7). However, value $RC = 200\,\mathrm{J kg^{-1}}$ is not inferior to this parameter for Gd foil with thickness of 0.215 mm, received by cold rolling [21].

4. Conclusion

GdTbDyHoEr powder of high-entropy alloy produced by grinding a fast-quenched tape of this alloy in a grinding mill was studied. It has hexagonal structure, the average size of crystallites is approximately 26 nm. As temperature drops, paramagnetic–helicoidal antiferromagnetic–ferromagnetic magnetic phase transitions are implemented in series in the powder. Neel temperature is 178 K. At $T < T_N$ the external magnetic field induces metamagnetic transition HAFM-FM. The presence of magnetic phase transitions executed via formation of various intermediate magnetic phases, the temperature range of existence of which depends on the value of the external magnetic field, is the reason for high value of cooling capacity, which is not inferior to the similar value for Gd foil produced by cold rolling. Therefore, GdTbDyHoEr powder of high-entropy alloy may be treated as a promising material for working material of a magnetic refrigerator.

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Conflict of interest

The authors declare that they have no conflict of interest.

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