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Critical indices of phase transitions and magnetic entropy in PrDyFeCoB microwires

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Microwires based on the PrDyFeCoB alloy in a field of 0−2 T are characterized by the presence of both positive and negative magnetocaloric effects (MCE) in the temperature ranges of 300−340 and 200−240 K, respectively. The low-temperature negative MCE is caused by the transition between the ferromagnetic and spin-glass states of the alloy, and the high-temperature MCE occurs during the spin-reorientation transition as a result of the competition between the shape anisotropy and volume anisotropy. The maximum relative cooling power was RCP = 0.007 J/g in a field of 2 T. The values of the obtained critical coefficients indicate that at the transition temperature to the spin-glass state, the spin ordering is two-dimensional, described by the Ising model.

Keywords: polycrystalline microwires, rare earth alloys, magnetic entropy, magnetoelastic anisotropy, Curie temperature, magnetocaloric effect, critical indices.

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1. Introduction

The magnetocaloric effect means that during a spin phase transition, for example, in the Curie point, a ferromagnetic exchanges heat with the environment in an isothermal mode or his temperature varies in an adiabatic mode of variation of the magnetic field [1,2]. This phenomenon can be used for creating new-generation refrigerators, which do not require a poisonous gas, are environmentally-friendly and their efficiency is much higher than that of gas machines. In another limit case, with a gradual isothermal increase or decrease of a value of the external magnetic field, the temperature of a sample remains unchanged and it is in equilibrium with a thermostat. At the same time, a magnetic component of entropy (ΔS_M) is changed, since there is exchange of heat with the environment. The value of entropy change is mostly influenced by processes that affect fully disordered states of the system such as paramagnetic or spin-glass states. The spin-glass phases are observed in PrDyFeCoB amorphous-crystallite microwires when transiting from the ferrimagnetic state [3]. Disorientation of the spins and variation of exchange interaction between them can cause the magnetocaloric effect in the PrDyFeCoB alloy. The similar effect was observed in metamagnetic alloys FeRh [4] and $Ni_{2+x}Mn_{1-x}Sn$ [5]. A high number of scientific studies was dedicated to investigating the magnetocaloric effect in bulk samples of the alloys RE-TM-B (RE — rare earth elements, TM — transition metals, B — boron) [6–12]. Studies of micromagnets that exhibit the magnetocaloric properties are less common in the literature. In the microwires $Pr_{1.3}Nd_{0.7}Fe_{17}$ and $Pr_{1.5}Nd_{0.5}Fe_{17}$ that have a rhombohedral structure of the type 2−17, the maximum change of the magnetic component of entropy is 4.31 J/kg · K [13]. The Curie temperature $T_C = 307$ K that is close to the room temperature as well s a high value of the relative cooling power parameter RCP = 487 J/g is demonstrated by the $Pr_{1.3}Nd_{0.7}Fe_{17}$ alloy [7].

One of the trends of increasing magnetic cooling efficiency is creation of internal mechanical stresses that affect magnetostriction anisotropy and the Curie temperature interval. It is found that a change of orientation of a substrate of the Gd films, which results in origination of mechanical stresses at the interface, significantly affects the value of the magnetocaloric effect [14]. It can be assumed that the microwires made by fast melt solidification are characterized by high levels of internal mechanical stresses, thereby contributing to the MCE increase. Among other things, the microwires are attractive as being a working media of the magnetic refrigerators, since a large surface area of the microwire array provides intense heat exchange with the environment [15–17]. A thermodynamic approach to calculating the magnetic part of anisotropy consists of taking into account magnetization M and a rate of its variation with the temperature. If the derivative $\partial M/\partial T$ depends only on a spin ordering degree, the MCE would be the same in all the materials and depend only on a value of the spin and a density of atom spins. However, a remagnetization process is controlled by exchange interactions and an anisotropy field. Therefore, it is important for the MCE value expressed as the entropy change in which way exactly the spins are ordered and which exchange interaction binds them. The exchange interaction in solid bodies is described by existing models of Heisenberg, Ising and their numerous modifications for different dimensionality. Therefore, a phenomenological determination of critical indices of the magnetic-ordered states and their transitions into the disordered states of the spins is important for understanding physical basics of the MCE.

The aim of the study was to comparatively analyze the critical indices of the spin states and the magnetocaloric effect in the polycrystalline microwires of the PrDyFeCoB alloy as well as to analyze variation of the magnetic part of entropy and the relative cooling power value.

2. Samples and experimental methods

The PrDyCoFeB microwires are manufactured by hanging drop melt extraction (HDME), which is based on fast extraction of a liquid metal from a suspended droplet by its contact with a sharp edge of a fast rotating water-cooled brass disk. Under effect of centrifugal forces, the drop was drawn into thin microwires, which quickly solidified due to intense cooling ($\sim 10^6$ K/s) [3,18] (Figure 1). The produced microwires (Figure 1) had a length 5–60 mm and a diameter 30–300 μm.

The measurement of the magnetic moment of the microwires in the SQUID magnetometer MPMS XL Quantum Design. The experiment was carried out in the temperature range from 2 to 350 K. In all the experiments, a direction of the main axis of the microwire coincided with the direction of the external magnetic field, since this very configuration of the sample provides maximum variation of the magnetic moment during the spin-reorientation transition described in the literature [3]. A field dependence of magnetization M was measured by gradually increasing the external magnetic field at the constant cryostat temperature.

The dependence of a longitudinal magnetic moment on the temperature was recorded by two methods: 1) FC („Field-Cooling“, cooling in the presence of the external magnetic field); 2) ZFC („Zero Field Cooling“, cooling in the absence of the external magnetic field). When using the FC method, the sample was first cooled in the strong external magnetic field (0.5 T) and then heated in the much smaller magnetic field (0.01 T), which did not destroy the state created by a thermomagnetic history. In doing so, the magnetic moment was measured. When using the ZFC method, the sample was pre-cooled in the absence of the external magnetic field and then heated as well, measuring the magnetic moment in the weak external magnetic field (0.01 T).

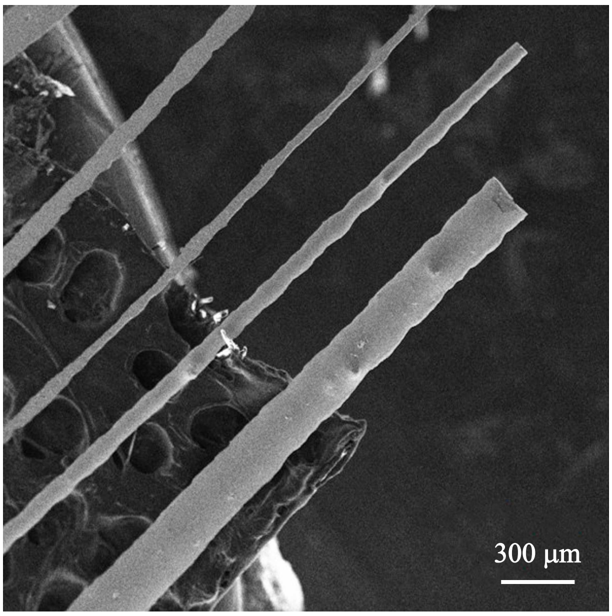

Figure 1. SEM-images of the PrDyCoFeB microwires on the substrate, which are obtained in a scanning electron microscope.

3. Experimental results and discussion

Figure 2 shows a spectrum of X-ray diffraction of the PrDyCoFeB microwires (Figure 2). The microwires have a polycrystalline structure with a basic magnetic phase 2-14-1, in which a portion of praseodymium y and a portion of iron x are varied in accordance with the formula $(Pr_yDy_{1-y})_2(Fe_xCo_{1-x})_{14}B$ [19], and which also has a low-magnetic Laves phase $Dy(Fe_xCo_{1-x})_2$.

Figure 3 shows the field dependence of the magnetic moment $m(H)$ of the microwire, which is obtained during isothermal variation of the external magnetic field from a positive-value range into negative values and vice versa for ~ 1 h. This field sweep mode provides relaxation of magnetization and isothermal magnetization of the sample. The PrDyCoFeB microwires have a typical ferromagnetic hysteresis loop with a high value of the coercive force $H_C \sim 10$ kOe (Figure 3).

Figure 4 shows the temperature dependences of magnetization $M(T)$ of the microwire, which are recorded in the modes FC and ZFC. For the PrDyCoFeB microwire, the dependences of FC and ZFC differ within the temperature range from 2 to 195 K (Figure 4). At the temperature of 195 K and higher, the curves of FC and ZFC coincide, therefore, $T_B = 195$ K can be interpreted as a temperature of magnetization blocking in the PrDyCoFeB microwire, thereby indicating that the microwire has ferromagnetic nanograins included in the basic matrix.

In order to obtain the magnetic part of entropy, we have obtained a series of the field dependences of magnetization $M(H)$, which are recorded at the constant temperatures and a slow sweep rate for the external magnetic field

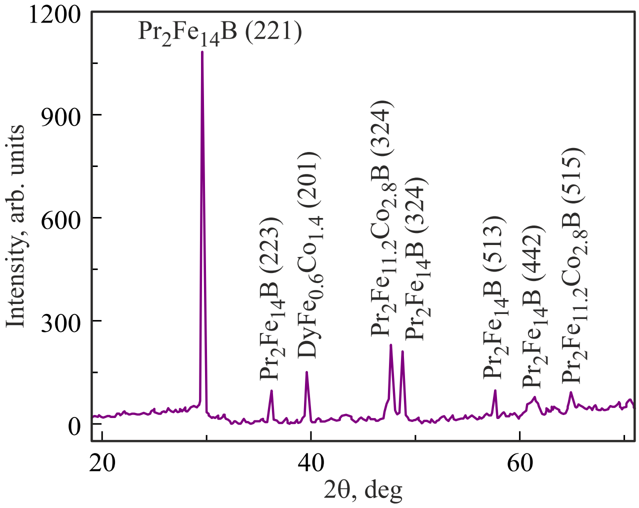

Figure 2. XRD spectra of the PrDyCoFeB microwires.

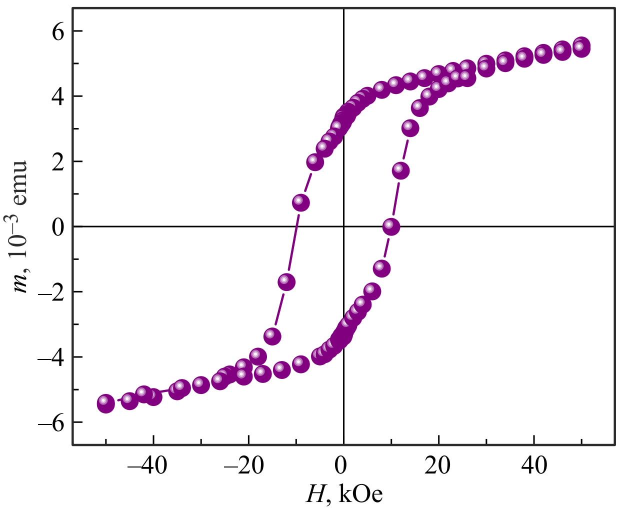

Figure 3. Field dependence of the magnetic moment m of the PrDyCoFeB microwire at the temperature $T = 300$ K.

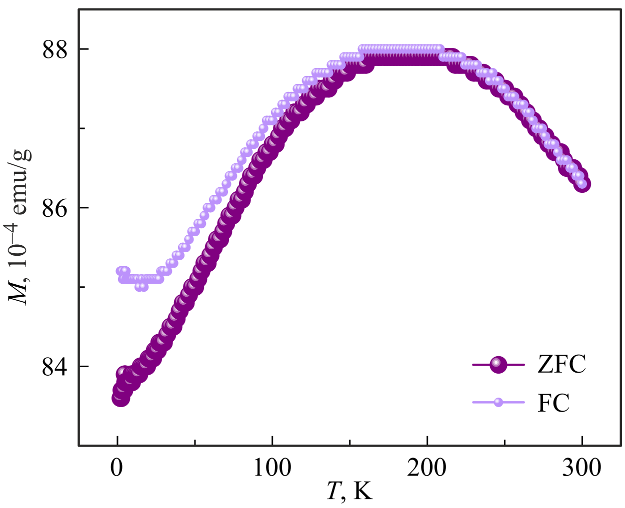

Figure 4. Temperature dependences of magnetization M of the PrDyCoFeB microwire, which are recorded in the field of 0.5 kOe in the modes ZFC (Zero Field Cooling) and FC (Field Cooling).

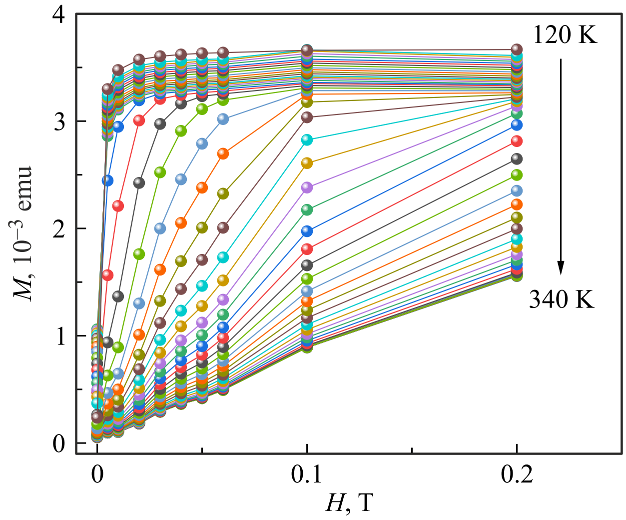

Figure 5. Isothermal dependences of magnetization M of the PrDyCoFeB microwire on the external magnetic field applied along the microwire axis, at the various temperatures.

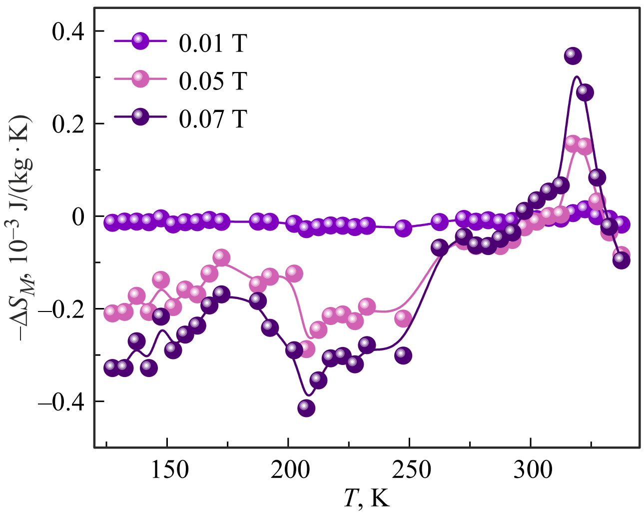

Figure 6. Temperature dependence of variation of the magnetic part of entropy of the PrDyCoFeB microwire in the various magnetic fields.

~ 0.0033 T/min. Figure 5 shows examples of the dependences of magnetization $M(H)$ of the PrDyCoFeB microwire within the temperature range 120–340 K, since this range encompasses the temperature of magnetization blocking T_B and the spin-reorientation transition in the PrDyCoFeB microwire, which is previously detected in the study [3].

A calculation of changes of full entropy S of the system is based on the Maxwell equation that specifies a dependence between changes of entropy and the magnetic moment [20,21]:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H. \quad (1)$$

Magnetocaloric properties of the microwires PrDyCoFeB and Gd

PrDyCoFeB microwire (when $H = 0.07\,T$)		
When $T = 207\,K$	$-\Delta S_m \sim -0.4\,mJ/kg \cdot K$	RCP $\sim 0.04\,J/g$
When $T = 317\,K$	$-\Delta S_m \sim 0.35\,mJ/kg \cdot K$	RCP $\sim 0.007\,J/g$
Gd microwire (when $H = 9\,T$) [22]		
When $T = 292\,K$	$-\Delta S_m \sim 16.9\,J/kg \cdot K$	RCP $\sim 0.66\,J/g$
When $T = 312\,K$	$-\Delta S_m \sim 15.4\,J/kg \cdot K$	RCP $\sim 0.28\,J/g$

The Maxwell relationship can be used to determine the value of the magnetocaloric effect that is determined by a contribution by specific magnetic entropy ΔS_M [20,21]:

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH. \quad (2)$$

In order to simplify processing of the empirical data, the equation (2) can be reduced to a discrete form, since during the experiment the changes of the temperature T and the external magnetic field H are of a discrete type.

$$\Delta S_M(T,H) = \sum_i \frac{M_{i+1}(T_{i+1},H) - M_i(T_i,H)}{T_{i+1} - T_i} \Delta H, \quad (3)$$

where $M_i(T_i,H)$ — magnetization at the temperature T_i, $M_{i+1}(T_{i+1},H)$ — magnetization at the temperature T_{i+1}. Figure 6 shows the temperature dependence of variation of the magnetic part of entropy of the PrDyCoFeB microwire in the various external magnetic fields.

The PrDyCoFeB microwire (Figure 6) exhibits a minimum (the temperature range 200–250 K) and a maximum (the temperature range 300–340 K) of entropy, thereby indicating that there is the negative and the positive effect, respectively. The positive magnetocaloric effect (heat absorption) can be caused by the spin-reorientation transition in crystallite inclusions of the tetragonal phase. The negative magnetocaloric effect (heat release) can be caused by the spin-reorientation Almeida–Thouless transition between the spin-glass state and the ferrimagnetic state, which is observed in the same temperature range [3].

The area of the peak $-\Delta S_M(T)$ is proportional to relative cooling power (RCP):

$$\text{RCP} = -\Delta S_m \Delta T_{1/2}, \quad (4)$$

where $\Delta T_{1/2}$ is a half-width of the maximum on the dependence $-\Delta S_M(T)$. Table shows the calculated RCP values for the PrDyCoFeB microwires as well as for the Gd microwires, which were previously obtained in the study [22].

The RCP values in the Gd microwires exceed RCP in the PrDyCoFeB microwires by two orders. This difference can be related to different types of exchange interaction that orders the spins in the microwires Gd and PrDyCoFeB.

A geometry of exchange interaction and the spin structure are usually determined by applying an Arrott method that is based on a molecular-field Weiss theory [23,24]. This analysis is based on an Arrott–Noakes equation:

$$(H/M)^{1/\gamma} = \frac{(T - T_c)}{T_c} + \left(\frac{M}{Mr}\right)^{1/\beta}, \quad (5)$$

where γ and β are critical parameters that characterize the nature of spin ordering in the ferromagnetic. Plotting the field dependences of magnetization in the coordinates $M^{1/\beta}(H/M^{1/\gamma})$ allows one to determine the parameters γ and β, and, based on their values, make conclusions about the two-dimensional, three-dimensional or more complicated ordering of the spins. To do this, from the series of the field dependences of magnetization a dependence is found that is straightened in the mentioned coordinates, fitting the values of γ and β, which are required for its straightening. In addition to information about spin ordering, this method also allows determining the transition temperature, at which it is straightened in the coordinates $M^{1/\beta}(H/M^{1/\gamma})$ with the respective critical coefficients.

The field dependences shown in Figure 5 were reduced to the coordinates $M^{1/\beta}(H/M^{1/\gamma})$ with the respective coefficients $\beta = 2$ and $\gamma = 1$ for a mean-field model, $\beta = 0.325$ and $\gamma = 1.24$ that correspond to the Ising model, $\beta = 0.365$ and $\gamma = 1.386$ for the Heisenberg model. The obtained Arrott curves are shown in Figures 7–9, respectively.

The values of the obtained critical coefficients indicate that in the microwires at the temperature, at which the spin-glass state is observed, spin ordering has a two-dimensional nature described by the Ising model. The value of the temperature, at which the Arrott curves are straightened, is $\sim 236\,K$, which is close to the temperatures values of 239 K, where the spin-glass state was observed in our study [3].

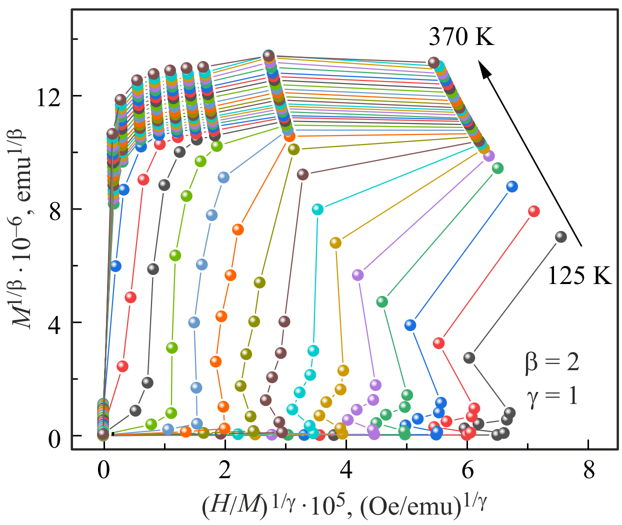

Figure 7. Arrott curves within the temperature range 125–370 K. The critical coefficient $\beta = 2$ and $\gamma = 1$ correspond to the mean-field model. The curves are not straightened when using this model.

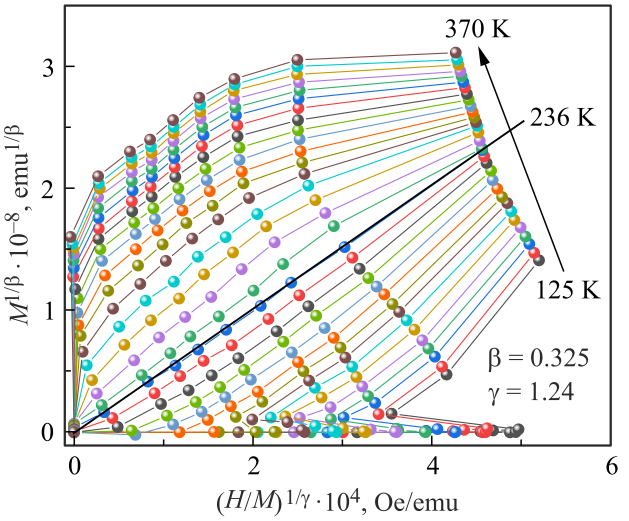

Figure 8. Arrott curves within the temperature range 125–370 K. The critical coefficients $\beta = 0.325$ and $\gamma = 1.24$ correspond to the Ising model. The curves are straightened at the temperature $T = 236$ K.

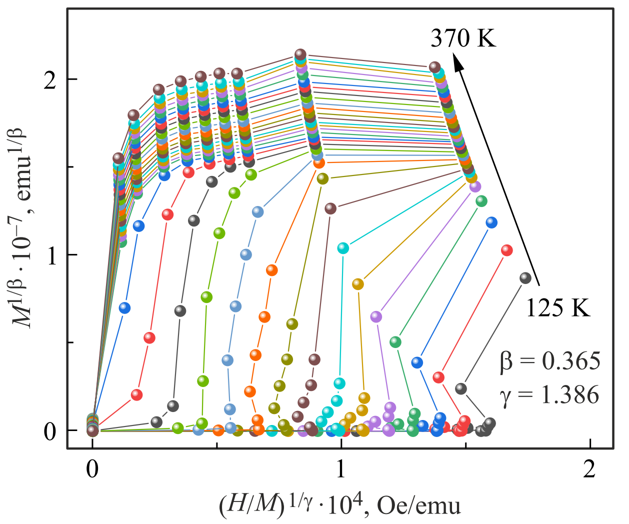

Figure 9. Arrott curves within the temperature range 125–370 K. The critical coefficients $\beta = 0.365$ and $\gamma = 1.386$ correspond to the Heisenberg model. The curves are not straightened when using this model.

4. Conclusions

The PrDyFeCoB-based microwires are characterized by the wide loop of magnetic hysteresis with the coercive force of 10 kOe and the presence of the positive and the negative magnetocaloric effect within the temperature range 300–340 and 200–240 K, respectively. The maximum value of relative cooling power in the PrDyFeCoB microwires, which is obtained in the present study and is RCP = 0.007 J/g, turned out to be by two orders of magnitude less than that in the Gd microwires. However, the magnetocaloric effect within the room temperatures makes it possible to apply the PrDyFeCoB microwires as a working body of a refrigerator. The critical coefficients indicate that the spin correlations in the PrDyFeCoB microwires at the temperature of the spin-glass state have the two-dimensional behavior that corresponds to the Ising model.

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Conflict of interest

The authors declare that they have no conflict of interest.

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