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Long-term effects of cyclic magnetic fields on the magnetocaloric properties of the $Ni_{43.18}Mn_{45.15}In_{11.67}$ Heusler alloy

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The thermal expansion ($\Delta l/l_0$), magnetocaloric effect (Delta ΔT_{ad}) and the magnetostriction (λ) of a polycrystalline sample of the $Ni_{43.18}Mn_{45.15}In_{11.67}$ Heusler alloy were studied. A correlation has been established between the magnetocaloric effect and magnetostriction. The smaller value of the MCE in the cooling run can be explained by the smaller contribution of the lattice subsystem to the total measured MCE. It is found that the long-term action of the cyclic magnetic field results in a decrease in the value of Delta ΔT_{ad} in the region of the first-order magnetostructural phase transition. The virgin properties of the alloy can be restored by transformation the sample to the austenite phase. The Heusler alloy $Ni_{43.18}Mn_{45.15}In_{11.67}$ can be used as a working body in magnetic cooling technology, provided that the alloy periodically transforms to the austenite phase.

Keywords: Heusler alloys, thermal expansion, magnetocaloric effect, magnetostriction, thermal cycling, cyclic magnetic fields.

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1. Introduction

Magnetic refrigeration technology based on the magnetocaloric effect (MCE) was offered as an alternative to conventional gas-compressor refrigeration machines. Such machines are supposed to be more environmentally friendly (with higher energy class) that the existing types with freon as working fluid. A set of requirements is imposed to materials to be used as working body for the magnetic refrigeration process, and the main requirement is associated with huge importance of the magnetocaloric effect in the room temperature range [1–3]. For practical application it is necessary to add one more requirement. This is a stability of magnetocaloric properties under long-term cyclic field exposure. Therefore, the main focus will be made herein on the investigation of frequency response of magnetocaloric properties of a material to be uses as working body in the magnetic refrigeration process. The cyclic magnetic field investigations allow to provide conditions close to magnetic refrigerator operating ones.

Some compounds such as Gd-Si-Ge [4], La-Fe-Si-H [5] or Mn-Fe-P (As, Ge) [6] demonstrate giant MCE associated with first-order magnetostructural phase transition (MSPT) that allows to heat the compounds by applying an external magnetic field or to cool them down by field removal. Heusler alloys with shape memory effect Ni-Mn-Z (Z = Ga, Sn, In) exhibiting martensite-austenite MSPT [7] were proposed as promising materials for the magnetic refrigeration technology. Heusler alloys are interesting in that they exhibit large MCE values over a wide range of temperatures near room temperature, as well as an interesting combination of magnetic and structural phase transitions.

The paper describes the experimental study of magnetic and thermal properties of a polycrystalline Heusler alloy $Ni_{43.18}Mn_{45.15}In_{11.67}$ sample: measurements of the temperature and field dependences of MCE and magnetostriction in cyclic magnetic fields up to 8 T and the temperature dependence of thermal expansion in a permanent magnetic fields up to 8 T within 77−350 K. The effect of long-term exposure to cyclic field on the magnetic properties of $Ni_{43.18}Mn_{45.15}In_{11.67}$ in the first-kind MSPT region was also investigated.

2. Experiment procedure

The sample under study was prepared by argon atmosphere arc melting. Then homogenizing annealing at $T = 900°C$ during 48 h in vacuum was performed. The accurately weighed nominal feed composition corresponds to the chemical formula $Ni_{43}Mn_{46}In_{11}$, while the actual composition measured by the wavelength dispersive X-ray spectroscopy method corresponds to $Ni_{43.18}Mn_{45.15}In_{11.67}$. The requirement to specify the elemental composition accurately is driven by the fact that physical properties of Heusler alloys are extremely sensitive to the elemental composition variation [8,9]. For example, in Ni_2MnGa, increased Ni concentration by 10 atom percents at the expense of Mn with constant atomic percentage of Ga

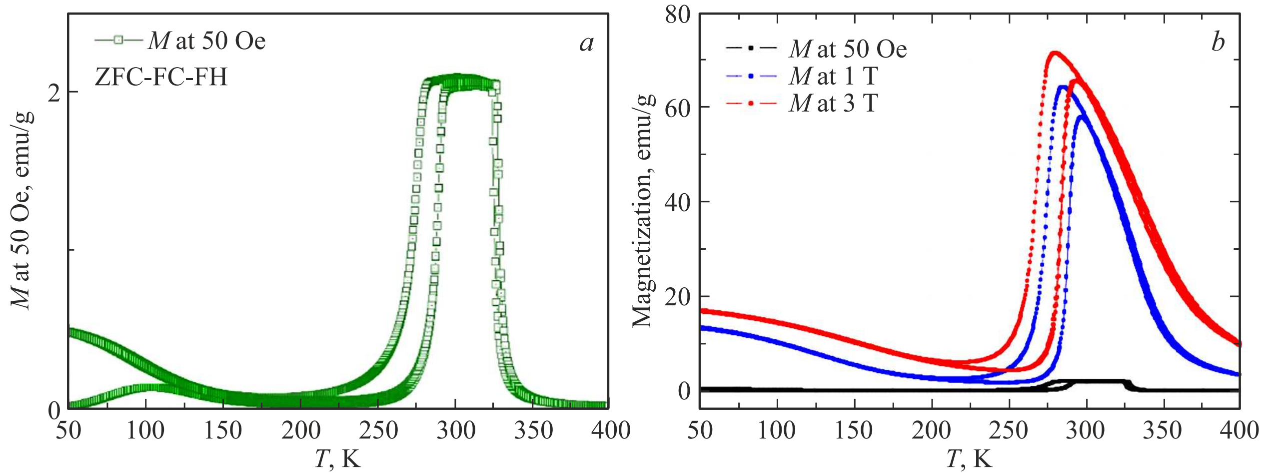

Figure 1. Alloy magnetization $Ni_{43.18}Mn_{45.15}In_{11.67}$ in magnetic fields up to 3 T.

results in increasing martensitic transformation temperature from 200 K to 650 K [10].

magnetization was measured using Quantum Design, PPMS-9T system. Direct MCE measurements in cyclic magnetic fields were carried out by the modulation method [11]. The principle of the method is as follows: the material under study is exposed to a low-frequency cyclic magnetic field that induces temperature oscillations in the sample. The AC signal from the thermocouple bonded to the sample is recorded with high accuracy by a Lock-In. This technique allows to record temperature variation with an accuracy at least 10^{-3} K [12].

Thermal expansion and magnetostriction were measured by the strain-gauge method [13]. KFL-05-120-C1-11 type strain gauges were used for strain measurements. The sample dimensions were $3\times3.5\times1.8$ mm. For the measurements, one strain gauge was bonded to the test sample face, and the other one, temperature-compensating strain gauge, was bonded to a quartz plate. Both strain gauges were connected to the Wheatstone bridge. Resistance difference between the primary and compensating strain gauges was max. 0.1 Ω. The sample length change due to thermal expansion results in a resistance change of the sensing strain gauge that will throw the bridge out of balance. The difference of potential in the bridge was measured by a multimeter. The temperature change rate throughout the experiments was equal to 1.5 K/min. An adjustable magnetic system with magnetic field 1.8 T and magnetic field variation frequency 0.2 Hz was used as a cyclic magnetic field source. The sample was heated above T_C before each measurement.

3. Findings and discussion

The Figure 1 shows the magnetization-temperature dependence of the $Ni_{43.18}Mn_{45.15}In_{11.67}$ Heusler alloy measured in magnetic fields up to 3 T during heating and cooling. As shown in the Figure, there are two irregularities associated with ferromagnetic-paramagnetic phase transitions in the austenite phase with $T_C = 333$ K and with austenite-martensite magnetostructural phase transition with $A_s = 285$ K, $A_f = 292$ K, $M_s = 280$ K, $M_f = 267$ K (A_s and A_f are the start and end of austenite transformations, M_s and M_f are the start and end of martensite transformations). Within 200−290 K, clearly pronounced temperature hysteresis that is typical for such materials is observed and can be indicative of structural changes accompanying such transition [14–16].

To investigate the role of the structural subsystem in MCE, linear thermal expansion was measured in $Ni_{43.18}Mn_{45.15}In_{11.67}$ (Figure 2). The curves show that a stepwise linear sample expansion is observed in the MSPT region. The applied magnetic field results in the shift of the anomalies towards low temperatures and in the temperature hysteresis broadening ($\Delta T_{hys} = 8.5$ K; 8.7 K;

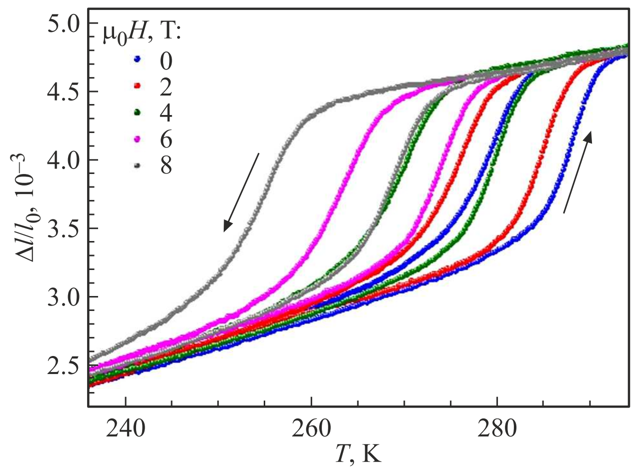

Figure 2. Linear thermal expansion vs. temperature of $Ni_{43.18}Mn_{45.15}In_{11.67}$ in various magnetic fields during heating and cooling runs.

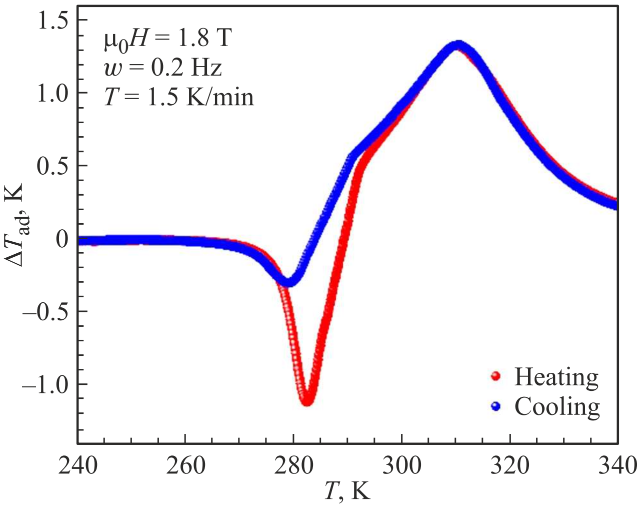

Figure 3. MCE vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.67}$ in the cyclic magnetic fields with an amplitude of 1.8 T during heating and cooling.

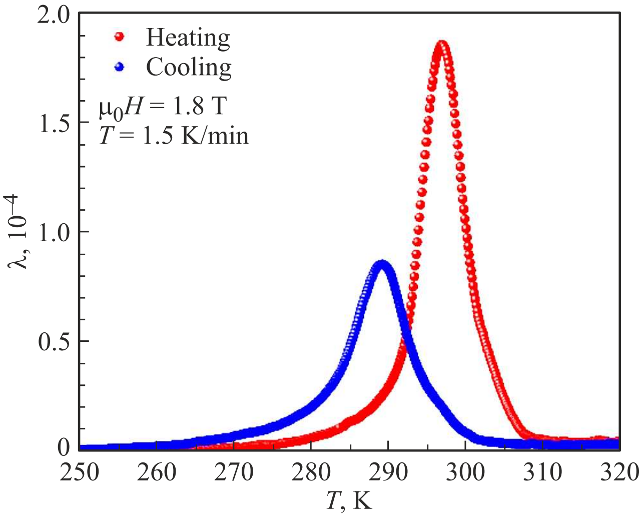

Figure 4. Magnetostriction vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.67}$ in the cyclic magnetic fields with an amplitude of 1.8 T during heating and cooling runs.

9.8 K; 10.2 K; 13.2 K; in magnetic fields 0 T, 2 T, 4 T, 6 T and 8 T, respectively).

Temperature dependences of MCE were measured in cyclic magnetic fields with a frequency of 0.2 Hz and amplitude of 1.8 T, (Figure 3). In the studied alloy, inverse (at MSPT) and direct (at magnetic phase transition) magnetocaloric effects are observed. MCE value in the MSPT region during heating ($\Delta T_{\max} = -1.1$ K) is three times higher than that during cooling run ($\Delta T_{\max} = -0.3$ K). In our previous study [17], one of possible explanations was provided for MCE value difference during heating and cooling runs. However, there is currently no common explanation of this effect.

To find the nature of such behavior, magnetostriction was measured in identical ambient conditions (cyclic magnetic fields, heating and cooling conditions) (Figure 4). As shown in the Figure, the same picture as for MCE is observed. Values of the magnetostriction also differ considerably in heating and cooling runs ($\lambda_{\max} = 1.87 \cdot 10^{-4}$ during heating and $\lambda_{\max} = 0.86 \cdot 10^{-4}$ during cooling), i.e. $\lambda_{\max}(heat.) \approx 2\lambda_{\max}(cool.)$. We have earlier established a strict correlation between the magnetocaloric effect and magnetostriction in the magnetostructural phase transition region [18,19]. Therefore, the lower MCE value during cooling may be explained by lower contribution of the lattice subsystem to the total MCE to be measured. Difference in values ΔT_{ad} and $\lambda_{\max}$ in heating and cooling runs are also different (in heating and cooling conditions, ΔT_{ad} differ approximately by a factor of 3 and $\lambda_{\max}$ differ approximately by a factor of 2). This suggests that not only structural contributions, but also magnetic contributions, differ in heating and cooling conditions. For comprehensive explanation of MCE distinctions in heating and cooling runs, further investigations are required, including the explanation of MSPT kinetics.

MCE behavior under continuously applied cyclic magnetic fields is an important issue associated with MCE investigation in the Heusler alloys. MCE value stability was measured in two different conditions: a set of measurements of MCE vs. temperature in cyclic magnetic fields and temporal dependencies of MCE under cyclic fields at desired temperatures.

Figure 5 shows several successively measured temperature dependences of MCE in cyclic fields in the MSPT region (thermocycling). Measurements were carried out as follows: temperature dependences of MCE were measured in 1.8 T magnetic field during heating. After transition into the austenite phase, the sample was cooled in the zero magnetic field. Thus, 4 temperature dependence curves were

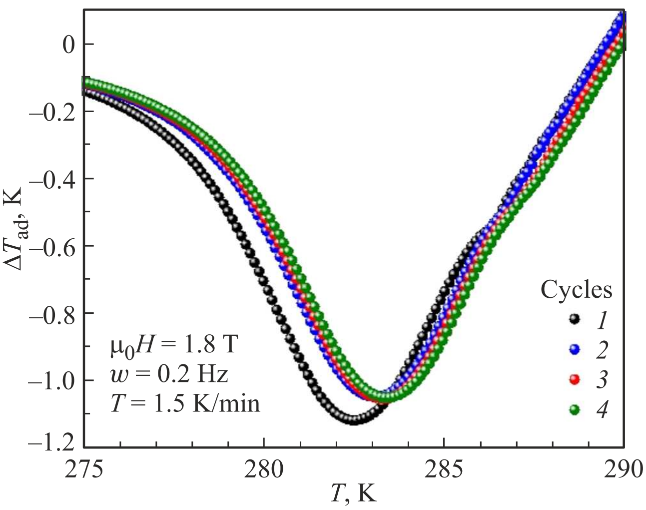

Figure 5. MCE vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.6}$ in 1.8 T magnetic field.

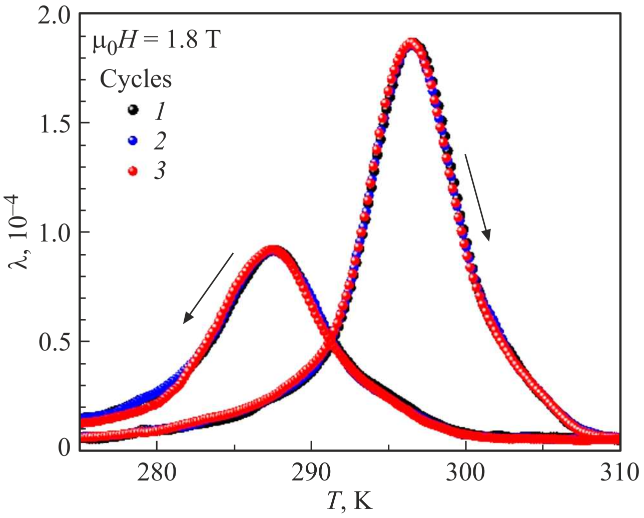

Figure 6. Magnetostriction vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.6}$ in 1.8 T magnetic field.

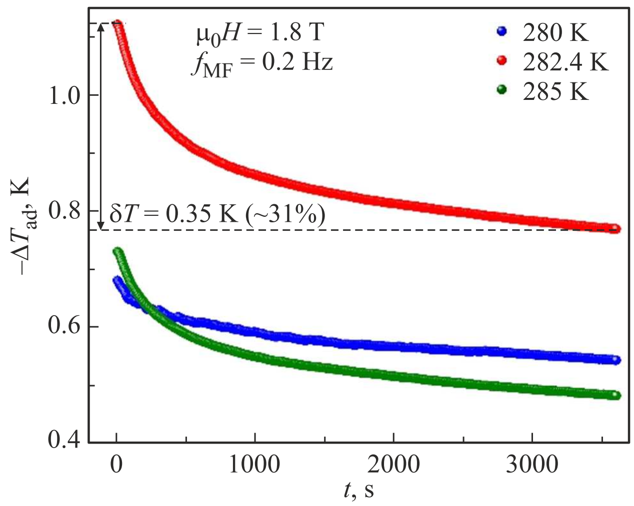

Figure 7. MCE vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.67}$ in 1.8 T cyclic magnetic field in the magnetostructural phase transition region.

recorded. It is apparent that the MCE value varies between cycles. Measurements of magnetostriction vs. temperature (Figure 6) were carried out under the same conditions, and difference in the values were not observed as well.

Quite different behavior is observed in measurements at a fixed temperature in the phase transition region. MCE in such conditions decreases considerable (Figure 7), magnetostriction also decreases, but to a lesser extent (Figure 8). Each curve was measured during 3600 s, the number of magnetic field application cycles was 720. The sample temperature was kept to within ± 0.05 K. In effect peak region ($T = 282.4$ K), MCE decrease is about 31%, and the magnetostriction magnitude ($T = 296.8$ K) decreases approximately by 9%. Difference in the degree of MCE and magnetostriction degradation is associated with the fact that peaks of ΔT_{ad} and λ are observed at different temperatures. After each such cycling, the sample was cooled to 77 K in the zero magnetic field and MCE vs. temperatures vs. and magnetostriction vs. temperature were measured. Temperature dependences of MCE measured during heating after cycling in magnetic fields at fixed temperature (Figure 9) in the phase transition region have additional irregularities that disappear in approach to the austenite phase. Temperature dependences of magnetostriction (Figure 10) measured in the identical conditions (after temporal dependence measurements) do not show any irregularities. Such behavior suggests that magnetic inhomogeneity regions occur in the sample, but they do not have clear pronounced structural irregularities. Disappearance of additional irregularities on the tempera-

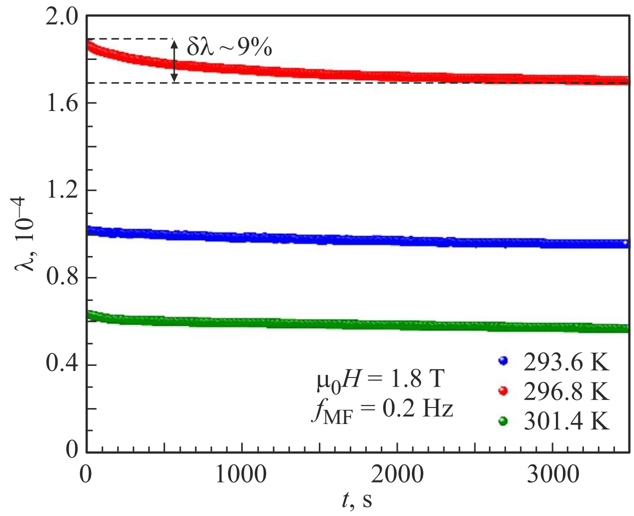

Figure 8. Magnetostriction vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.67}$ in 1.8 T cyclic magnetic field in the magnetostructural phase transition region.

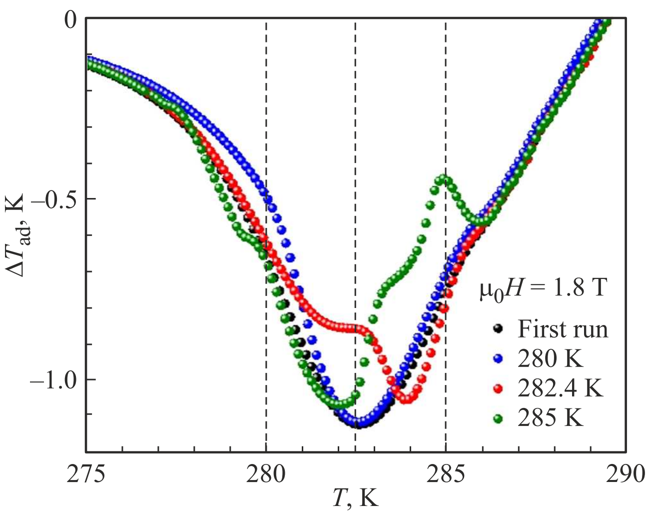

Figure 9. MCE vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.67}$ in 1.8 T field after the measurements at fixed temperature, and the initial curve.

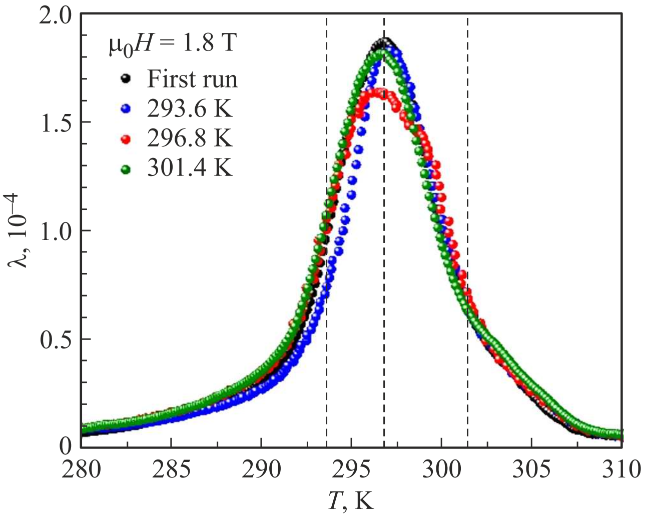

Figure 10. Magnetostriction vs. temperature in $Ni_{43.18}Mn_{45.15}In_{11.67}$ in 1.8 T field after the measurements at fixed temperature, and the initial curve.

ture dependences of MCE during transition to the austenite phase also explains the reason why there is no MCE value variation during the measurement of temperature dependences of MCE (Figure 5) under the cyclic magnetic field. In each MCE-temperature dependence measurement cycle, the sample is transformed into the austenite phase, where initial properties are restored, and in the following temperature dependence measurement cycles, we have the sample with its initial properties. Differences in the degree of MCE and magnetostriction degradation is explained by the fact that irregularity peaks are observed at different temperatures.

4. Conclusion

Thus, in this work the effect of long-term cyclic fields on magnetocaloric properties of the $Ni_{43.18}Mn_{45.15}In_{11.67}$ polycrystalline Heusler alloy is studied. It has been found that 1.8 T long-term cyclic magnetic field exposure results in considerable decrease of the MCE value in the MSPT region. After the transition into the austenite phase, the initial magnetocaloric properties are restored. Correlation between the MCE and magnetostriction behavior in AC magnetic fields has been established. The findings suggest that such materials may be used as working body in the magnetic refrigeration process with such thermodynamic cycle, where full martensite-austenite transition occurs in the material in each working cycle.

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Conflict of interest

The authors declare that they have no conflict of interest.

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