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Effect of graphene on the mechanochemical activation of cobalt ferrite nanoparticles

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ABSTRACT

Cobalt ferrite nanoparticles were exposed to mechanochemical activation, with and without equimolar amounts of graphene nanoparticles, for time periods ranging from 0 to 12 h. Their structural and magnetic properties were detailed from Mössbauer spectroscopy and magnetic measurements. The Mössbauer spectrum corresponding to the unmilled cobalt ferrite powder was analyzed using 2 sextets, corresponding to the tetrahedral and octahedral sites of ferrites. The rest of the spectra was deconvoluted using an additional quadrupole-split doublet, with an abundance close to 30% and was assigned to superparamagnetic particles. Moreover, the spectra corresponding to milling with graphene at the longest times needed a third sextet, which could be assigned to iron carbide. The degree of inversion was determined from the Mössbauer spectra and found to decrease with milling time, both for the set with and that without graphene. The canting angle was derived and studied as function of the ball milling time for both sets of samples. Hysteresis loops were recorded at 5 K in an applied magnetic field of 5 T and was found to exhibit a wasp-waist shape. Magnetization was plotted as function of temperature in the range 5–300 K with an applied magnetic field of 200 Oe using zero-field-cooling-field-cooling (ZFC-FC) measurements. These made it possible to determine the blocking temperature of the samples. Our data exhibit new characteristics of the cobalt ferrite nanopowders milled with and without graphene nanoparticles.

1. Introduction

The incorporation of carbon in ferrite nanoparticles lattice may give rise to nanocomposite and new hybrid materials, which can find applications in bioengineering and energy field, such as controlled drug delivery, magnetic recording media, magnetic toners, magnetic resonance imaging, ferrofluids, as well as in electrochemical energy storage and supply.

The cobalt ferrite ($CoFe_2O_4$) is an inverse cubic spinel with the space group Fd-3m, where the occupancy of the interstices is inverted, such that all of the tetrahedral positions A are occupied by the trivalent ions, while the tetrahedral B sites are occupied by the remaining cations. The cobalt ferrite exhibits high coercivity, adequate saturation magnetization and stability when interacting with the environment [1–12]. Due to these characteristics, the cobalt ferrite finds outstanding applications as magneto-optical devices and in medicine. Furthermore, the cobalt ferrite magnetic nanoparticles have attracted considerable attention in the field of biomedicine, since there is the possibility of manipulation of the particles with applying an external magnetic field [13–28].

If two-dimensional graphene-based materials have been the subject of many investigations, zero-dimensional graphene (graphene nanoparticles) leaves room for future contributions. Indeed, nanoparticles possessing magnetic properties introduced in a non-magnetic graphene host combine both the benefits of the unique properties of graphenes and magnetization.

In this paper we report novel investigations of cobalt ferrite nanoparticles during mechanochemical activation by high-energy ball milling, with the alternate introduction of graphene in the milling nanopowder. These investigations were performed using Mössbauer spectroscopy and magnetic measurements. The hyperfine parameters were derived and studied as function of the ball milling time. The degree of inversion was monitored and the canting angle was plotted as a function of milling time during mechanochemical activation. Constricted hysteresis loops were evidenced and the blocking temperature was determined as function of the milling time.

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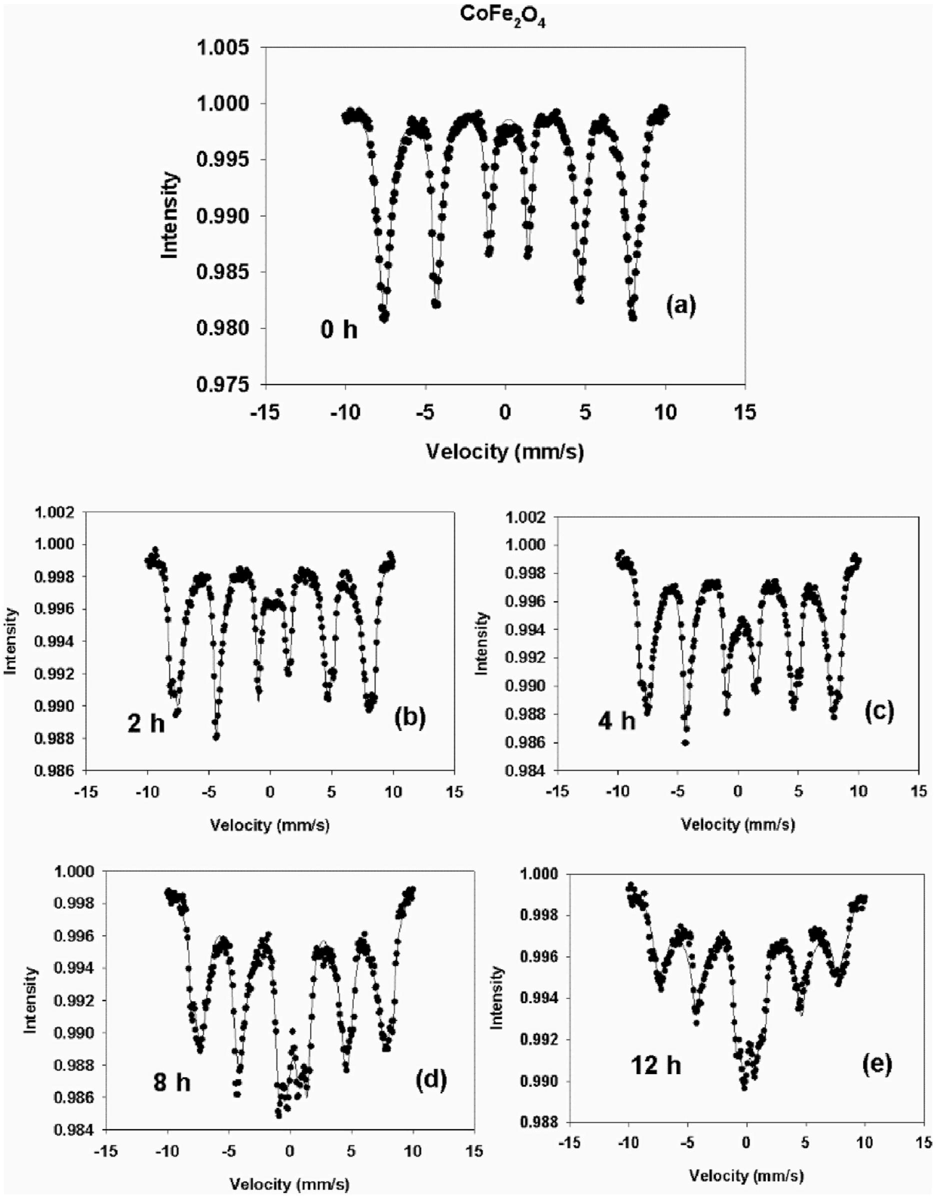

Fig. 1. Mössbauer spectra collected after ball milling cobalt ferrite for 0–12 h.

2. Materials and methods

Cobalt ferrite nanoparticles (Alfa Aesar, 50 nm particle size), with and without equimolar mixtures of graphene nanoparticles (SkySpring Nanomaterials, 1–5 nm particle size) were exposed to mechanochemical activation by high-energy ball milling for time intervals of 0–12 h.

Precursor powders were processed in a SPEX 8000 mixer mill for time periods starting from 0 to 12 h. The 8000 M Mixer/Mill is a high-energy ball mill that grinds up to 0.2–10 g of brittle samples. In our experiments the powder: ball mass ratio was 1:5. The balls and vial were made of stainless steel.

The room temperature Mössbauer spectra were recorded in the transmission geometry using gamma radiation emitted by a^{57}Co source diffused in a Rh matrix. The spectrometer was operated in the constant acceleration mode and the spectra for cobalt ferrite were taken after 0–12 h of ball milling time.

Hysteresis loop measurements were recorded with a Quantum Design SQUID magnetometer at a temperature of 5 K and an applied magnetic field of 5 T. The zero-field-cooling-field-cooling (ZFC-FC) was performed at 200 Oe (1 Oe = 10^{-4} T) and a temperature interval of

Table 1

Hyperfine parameters of cobalt ferrite nanoparticles, in the absence and presence of graphene, after different ball milling times. BMT is the ball milling time, H_{octa} and H_{tetra} are the hyperfine magnetic fields of the octahedral and tetrahedral sublattices, QS is the quadrupole splitting, $A_{doublet}$ is the relative abundance of the doublet and λ and θ are the inversion parameter and canting angle of the samples.

BMT (h)	H_{octa} (T)	H_{tetra} (T)	QS (mm/s)	$A_{doublet}$ (%)	λ	θ (deg)
0	51.207	47.830	–	–	1.00	40.44
2	51.481	47.912	0.801	16.2	0.91	36.03
4	51.240	47.425	0.740	20.6	0.87	50.65
8	50.900	46.696	1.330	30.9	0.80	59.75
12	50.700	47.700	1.100	13.7	0.75	60.65
0	51.207	47.830	–	–	1.00	40.44
2	50.100	47.050	1.200	22.8	0.95	66.58
4	51.100	47.100	0.815	20.2	0.62	76.05
8	51.760	47.100	0.750	32.6	0.50	71.10
26.5 (new phase)						
12	52.17	49.10	0.850	30.9	0.42	80.80
26.5 (new phase)						

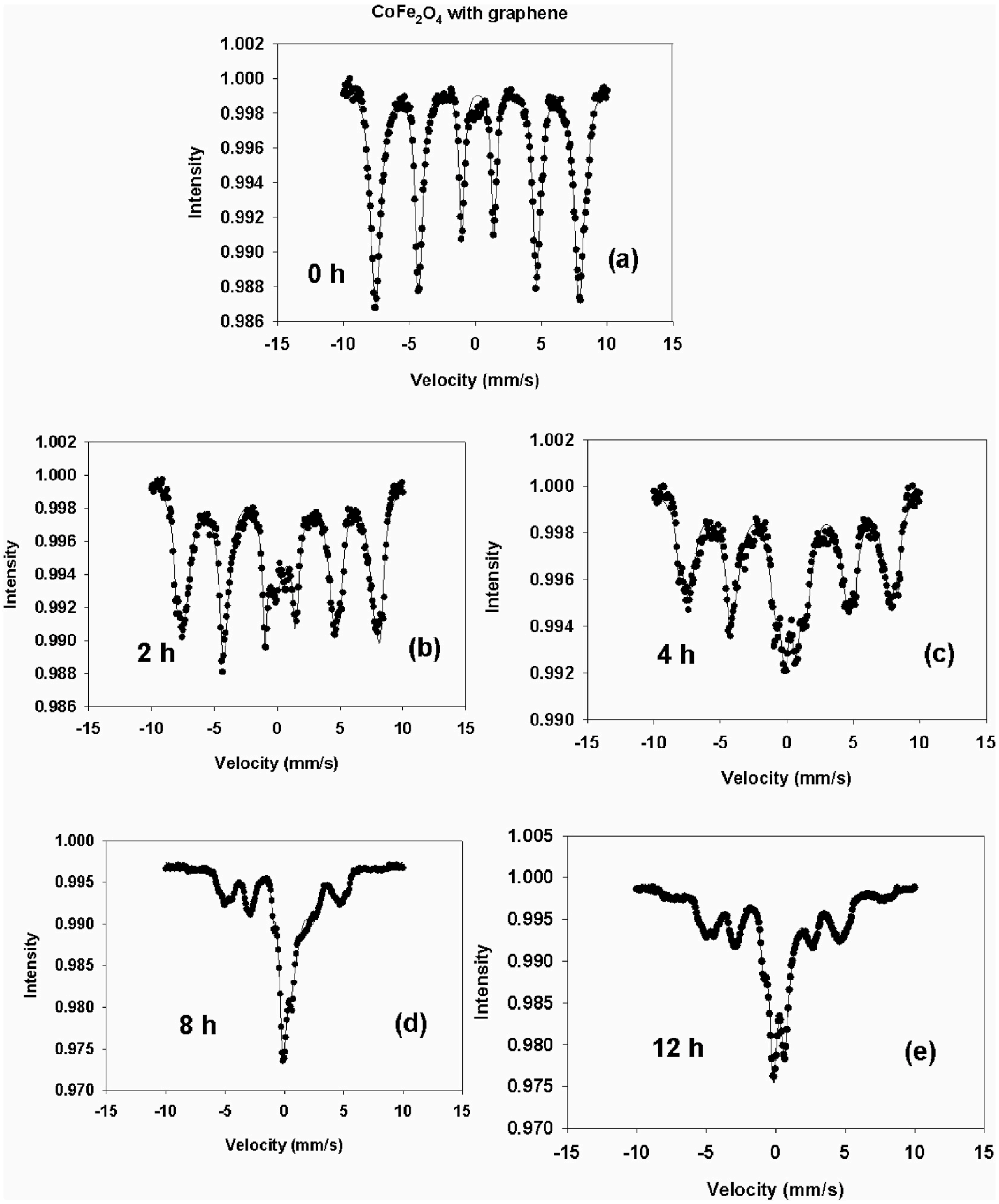

Fig. 2. Mössbauer spectra collected after ball milling cobalt ferrite and graphene for 0–12 h.

5–300 K.

3. Results and discussion

Fig. 1 (a)-(e) shows the room temperature transmission Mössbauer spectra for cobalt ferrite taken after 0–12 h of ball milling time. All spectra, both for pristine and milled samples, were fitted with 2 sextets, corresponding to the tetrahedral and octahedral magnetic sublattices (Table 1; estimated particle size 15 nm). The spectra corresponding to milled samples were analyzed using an additional quadrupole split doublet, which is indicative of the occurrence of superparamagnetism in the nanoparticles system (~30% abundance).

Fig. 2 (a)-(e) displays the Mössbauer spectra collected after ball milling for 0–12 h, with graphene nanoparticles added to the milling powders of cobalt ferrite.

It can be seen in Fig. 3 that the hyperfine magnetic field of the octahedral sites averages at about 51.1 T, while that of the tetrahedral sites takes values around 47.7 T. The quadrupole doublet has a quadrupole splitting of about 0.75 mm/s and a typical abundance of about 30%. A third sextet with a hyperfine magnetic field of 26.5 T was resolved for the spectra corresponding to graphene at long milling times and assigned to a carbon-rich phase, presumably iron carbide [25].

The $CoFe_2O_4$ structure can be written as $(Co_{1-\lambda}Fe_{\lambda})[Co_{\lambda}Fe_{2-\lambda}]O_4$, where λ is the fraction of the A sites occupied by Fe^{3+} cations, known as the degree of inversion. This parameter is given by the formula: $I_A/I_B = f_A/f_B \times \lambda/(2-\lambda)$, where I are the areal intensities of the two sextets, $f_B/f_A = 0.94$ at room temperature are the recoilless fractions, while the degree of inversion takes values $\lambda = 0$ for a normal spinel, $\lambda = 1$ for an inverse spinel and $\lambda = 2/3$ for a random distribution.

It can be seen in Fig. 4 that the degree of inversion λ decreases from the value of one to 0.75 after 12 h of milling, such that the material can be designed to take all forms from inverse to normal spinel structures. If graphene is added to the milling powders, the degree of inversion decreases again down to 0.42, such that mixed spinels are typically

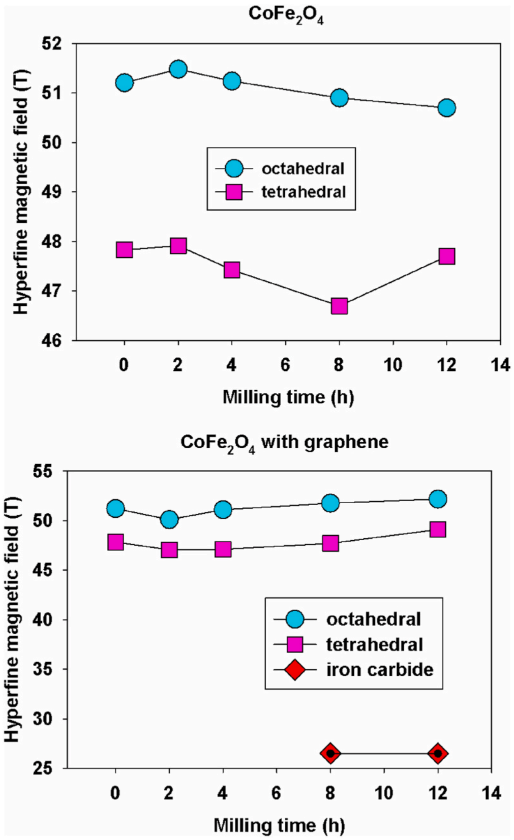

Fig. 3. Hyperfine magnetic field as function of ball milling time for cobalt ferrite nanoparticles, with and without graphene.

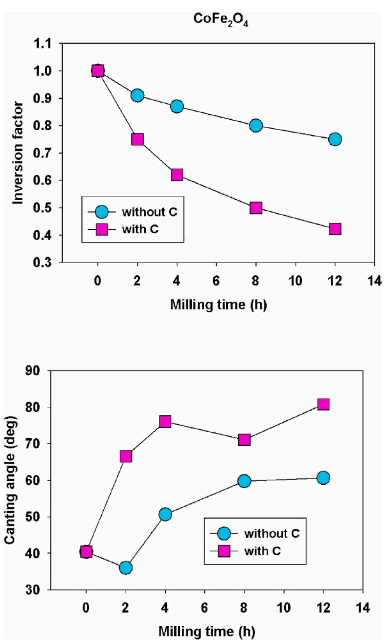

Fig. 4. Degree of inversion and canting angle for cobalt ferrite.

obtained.

A different parameter that can be derived from the Mössbauer spectra of the cobalt ferrite is the canting angle, which is the average angle between the direction of the hyperfine magnetic field and the direction of propagation of the gamma radiation. The canting angle is given by the formula: $\theta = \arcsin\,[3/2(I_2/I_1)/[1 + 3/4(I_2/I_1)]$. It can be seen in Fig. 4 that the canting angle of milled cobalt ferrite increases from 40.44° to about 60.65°, while the presence of graphene increases its value to 80.82°. This means that milling with graphene tends to orient the hyperfine field of the ferrite nanoparticles perpendicular to the direction of gamma ray propagation.

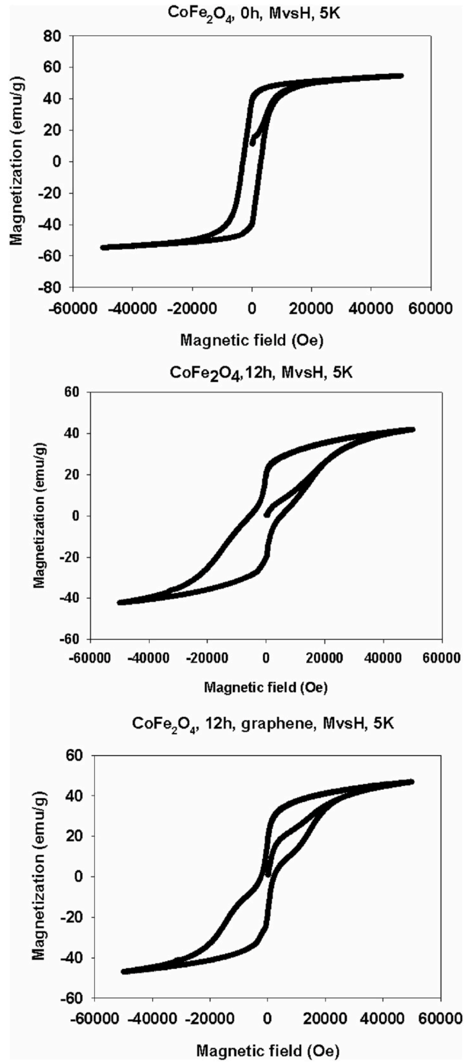

Fig. 5. Hysteresis loops recorded at 5 T and 5 K for cobalt ferrite, with and without graphene.

Fig. 5 shows the hysteresis loops recorded at 5 T and 5 K for the cobalt ferrite nanoparticles with the eventual addition of graphene in the mixing powders. It can be seen that these are constricted hysteresis loops [24] with a wasp-waist shape. We propose that this is due to spin reorientations, with domain wall motion and pinning of potential wells formed by directional order. Analyzing the squareness of the hysteresis loops we obtained that the ratio of the remanence to the saturation magnetization is less than 0.1, which means that the samples are in a multidomain state.

Fig. 6 displays the ZFC-FC curves for the magnetization versus temperature plot in an applied magnetic field of 200 Oe. The blocking temperature was estimated from the maximum of the ZFC curve and found to be close to 298 K and preserve a constant value for all samples in the set. This behavior is in contradistinction to the one for zinc ferrite [2], which showed a clear dependence of the blocking temperature on the milling time both with and without graphene.

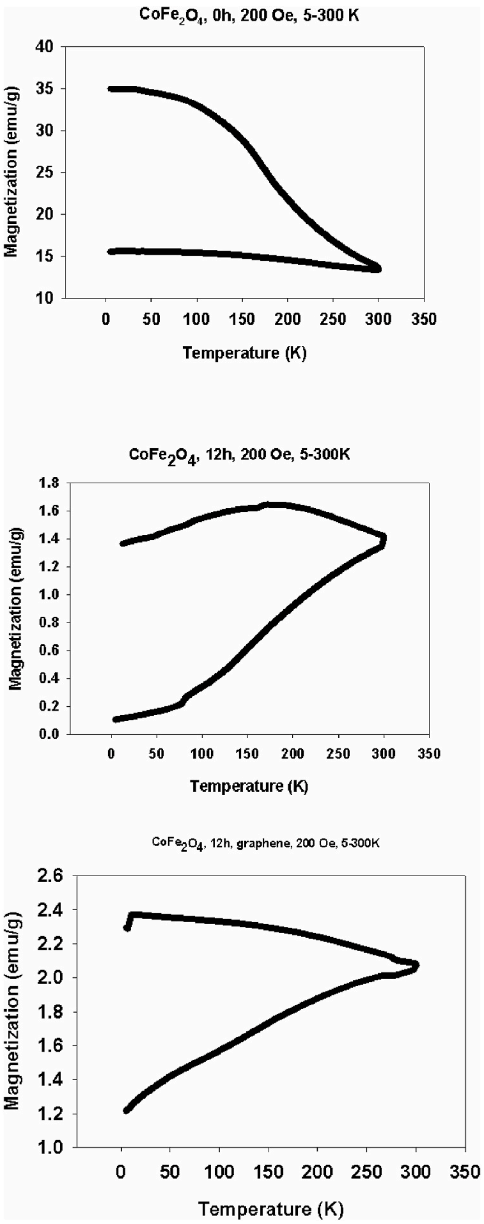

Fig. 6. ZFC-FC measurements at 200 Oe and 5–300 K of the cobalt ferrite with addition of graphene to the mixing powders subjected to different milling times.

4. Conclusions

In this work we successfully synthesized cobalt ferrite nanoparticles, with and without graphene, by high energy ball milling. The main results obtained from the Mössbauer spectroscopy and magnetism study are as follows:

(i) The hyperfine magnetic field of the tetrahedral and octahedral sites was studied as function of ball milling time. A quadrupole doublet was resolved due to the presence of superparamagnetic particles in system. A third sextet was obtained for the sample rich in carbon and was assigned to Fe atoms having an increased number of carbon atoms as nearest neighbors, presumably iron carbide.

(ii) The study of the degree of inversion as function of ball milling time demonstrated that spinels with inversions between 1 and 0.42 can be engineered for cobalt ferrite.

(iii) The canting angle increased when the content of graphene was increased.

(iv) A kink in the hysteresis loop was observed for the cobalt ferrite samples and assigned to spin reorientations.

(v) The blocking temperature was derived from ZFC and found to preserve the value for all samples in the set.

CRediT authorship contribution statement

Monica Sorescu: The author certifies that all five co-authors contributed to the work load as described in the present paper. **Jordan Jubeck:** The author certifies that all five co-authors contributed to the work load as described in the present paper. **Matthew Knauss:** The author certifies that all five co-authors contributed to the work load as described in the present paper. **Alice Perrin:** The author certifies that all five co-authors contributed to the work load as described in the present paper. **Michael McHenry:** The author certifies that all five co-authors contributed to the work load as described in the present paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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