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Magnetic response of bovine spleen

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Abstract

Bovine spleen has been used as a sample for deep magnetochemical investigation. Temperature dependence of the magnetic susceptibility and field dependence of the magnetization reveal a paramagnetic behaviour that violates the Curie law. The zero-field cooled magnetization and field cooled magnetization experiments show the bifurcation point at *ca* T_C = 20 K and the blocking temperature T_B = 10 K confirming a dominating portion of ferritin along with the organic tissue. There is a remnant magnetization at temperature below 20 K and the search for the magnetic hysteresis was positive.

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Introduction

Investigation of magnetic properties of several animal and/or human organs brought important information that some deposits of the iron oxides are present in them, at least in spleen (Boča *et al.* 2013; Kopáni *et al.* 2015) and brain (Kirschvink *et al.* 1992; Makohusová *et al.* 2014; Dlháň *et al.* 2018). These deposits consist of hematite α-Fe_2O_3 (antiferromagnetic), maghemite γ-Fe_2O_3 (ferrimagnetic) and/or magnetite Fe_3O_4 (ferrimagnetic); they coexist with wüstite FeO and various iron-oxides-hydroxides such as goethite FeOOH and ferrihydrite $5Fe_2O_3 \cdot 9H_2O$. The organs with the blood circulation also contain traces of hemoglobin and some amount of ferritin.

Ferritin is a globular protein of the external size of ca 12 nm with an internal cavity of ca 8 nm. This space serves as iron storage container and typically it is filled by the mineral core formed of ferrihydrite, along with some other iron-oxide minerals (Gálvez *et al.* 2008). About 4500 Fe^{3+} ions are stored in the ferritin globule. Ferritin is contained mostly in spleen, liver, and bone marrow. Several groups investigated magnetic properties of ferritin (Makhlouf *et al.* 1997; Brem *et al.* 2006). However, the actual data can depend upon the source such as the horse spleen ferritin or human spleen. In the present study, the bovine spleen has actually been subjected to magnetochemical studies.

Experimental

*Bovine spleen sample **1***

Sample extracted from the bovine spleen has been subjected to lyophilization. The powder-like material has been weighted into gelatine made container.

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Ferritin sample ***2***

Ferritin extracted from the horse spleen was purchased from Polysciences, Inc. (USA), Catalog #217. The certificated element content is N, 12.48 %; Fe, 15.50 %; P, 1.15 %; protein solids (including iron) 110.33 mg.cm^{-3}, solvent 0.15 M NaCl. Fe: 5.8 % in lyophilized sample (AAS).

Magnetic measurements

Solid samples **1** and **2** have been weighted into gelatine made container and inserted into the measuring chamber of the SQUID magnetometer (Quantum Design, MPMS-XL7). Temperature dependence of the magnetic susceptibility has been taken at small external field B = 0.1 T between T = 1.9 and 300 K. Magnetization measurements have been conducted at low temperature T = 2.0 and 4.6 K between B = 7 T and zero. The ZFCM/FCM data was taken as follows: the sample was cooled in the zero field to T = 2.0 K, then small field of B = 0.01 T has been applied and the magnetic data was acquired until T = 300 K (ZFCM curve); then the data taking continued in the cooling regime (FCM curve). Finally, the hysteresis loops have been taken between B = +5, 0, –5, 0, +5 T at a set of constant temperatures.

Results and Discussion

The magnetic susceptibility data of **1** at low temperature confirms the paramagnetic response (Fig. 1). Though the susceptibility decreases on heating it does not follow the Curie law since the susceptibility-temperature product function χT is not a straight line with the zero slope. The susceptibility curve crosses zero at T ~ 150 K which has an origin in the presence of the

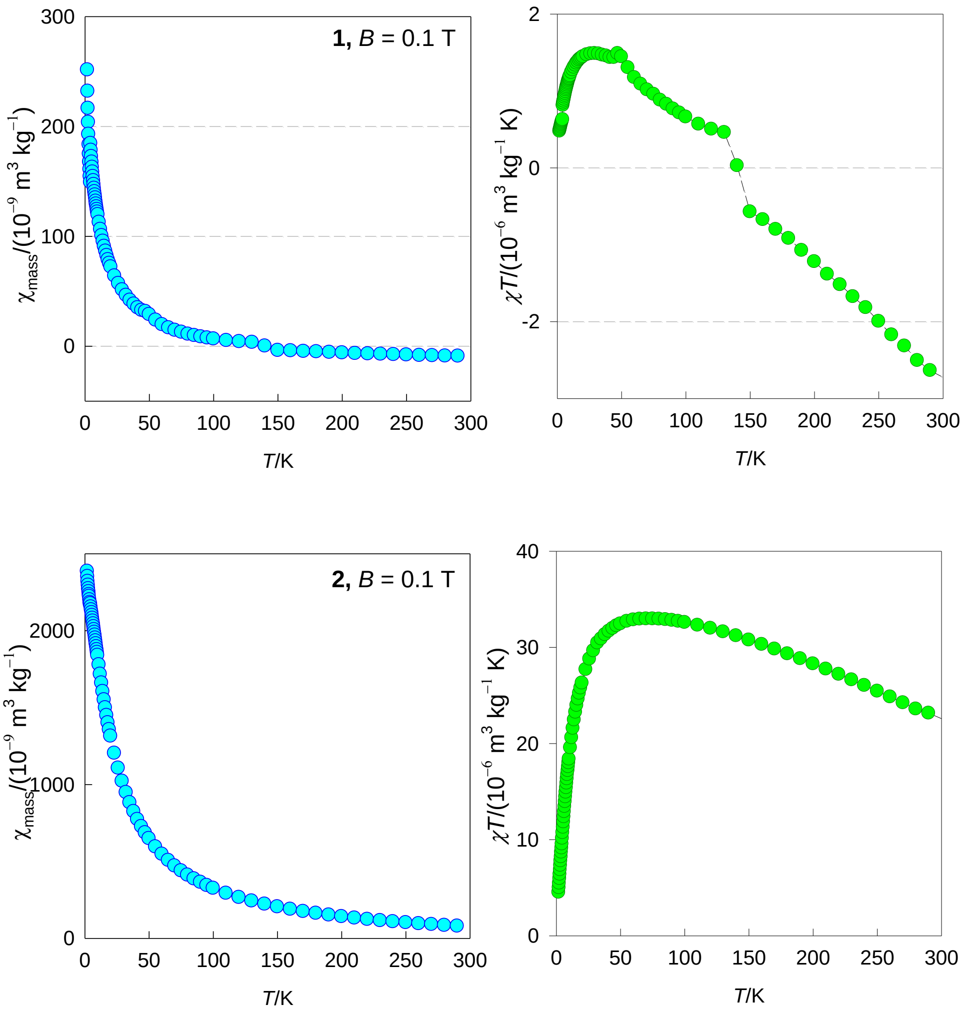

Fig. 1. Magnetic susceptibility (left) and the susceptibility-temperature product function (right) for the bovine spleen sample **1** and horse spleen ferritin **2**.

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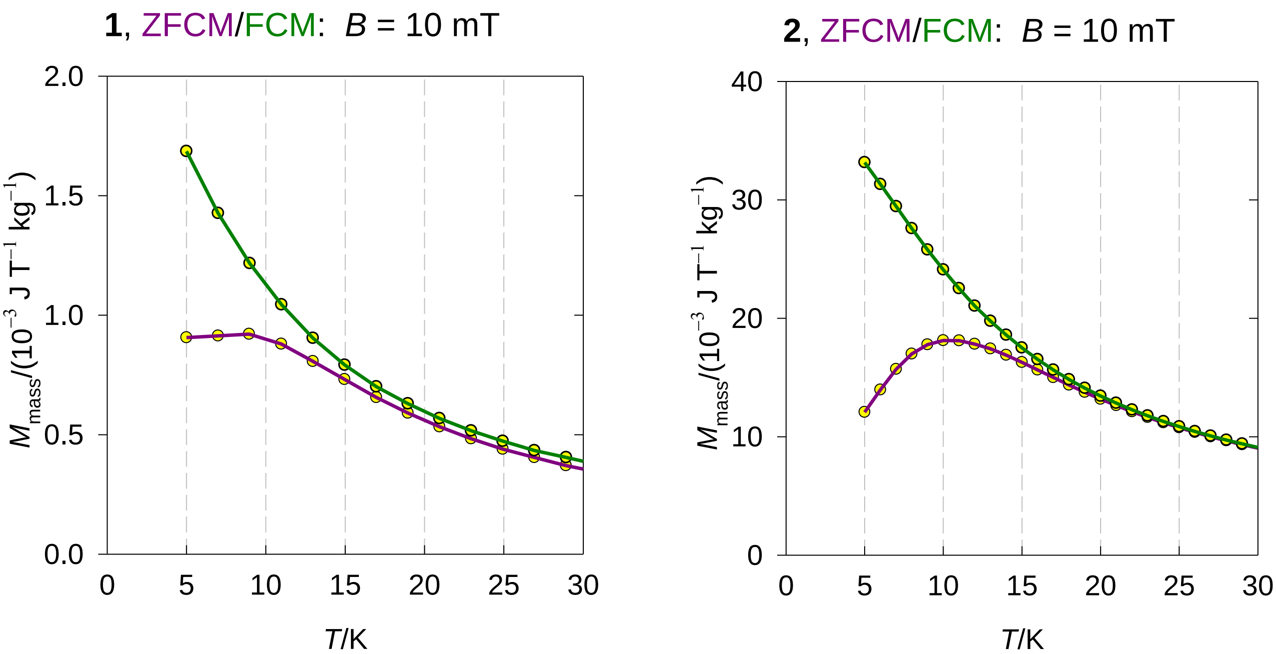

Fig. 2. ZFCM/FCM data for the bovine spleen sample **1** and horse spleen ferritin **2**. Lines are visual guide.

diamagnetic organic tissue. (Near zero signals the SQUID magnetometer is frustrated in fitting the recorded current/voltage to the equation of the perfect magnetic dipole.) There is a small hook at T ~ 50 K that refers to the *solidus-solidus* phase transition of the dioxygen present in the sample/container.

The above data displays a similarity with that recorded for the sample **2** (horse spleen ferritin). This sample brings only a paramagnetic response since the diamagnetism of the organic globule is suppressed by a strong paramagnetic signal of inorganic core of the ferrihydrite nature, $5Fe_2O_3 \cdot 9H_2O$ or FeOOH. In a harmony with expectations, the mass susceptibility of **2** is about an order of magnitude higher relative to **1**.

The ZFCM/FCM experiment for **1** shows that there exists a maximum at the ZFCM curve confirming a presence of the blocking temperature, T_B ~ 9 – 10 K, that characterizes the super-paramagnetism of nanosized objects (Fig. 2). This curve tends to coincide with the FCM record at critical T_C ~ 20 K that is the bifurcation point. However, small divergence of ZFCM/FCM curves survives until the room temperature (end of the data taking) which points to the presence of a minor portion of the ferro-/ferrimagnetic phase.

The above data resembles high similarity with those recorded for the horse spleen ferritin. Here the bifurcation point is exactly at T_C ~ 20 K and the blocking temperature of the super-paramagnetism is well identified at T_B = 11 K. Small discrepancies between **1** and **2** can be attributed to the super-ferromagnetism of **1**: the magnetism of an ensemble of magnetically interacting super-paramagnetic nanoobjects.

The magnetization data, taken at the field decreasing mode, shows that at the zero field some remnant magnetization survives (Fig. 3). This is much higher for **2** relative to **1**. The magnetization data at T = 7 T are far from saturation. There is an anomaly above B > 3 T and T = 2 K for **1** of unknown origin; this can be due to a multiphase composition of **1**. The magnetization data was fitted by using the Langevin function extended to the first- and second-order susceptibility

$$M_{\mathrm{mass}}(B,T) = M_{\mathrm{sat}} \cdot [\coth(y) - 1/y] + \chi_1 B + \chi_2 B^2 \quad (1)$$

for the argument

$$y = m_{\mathrm{p}} \mu_{\mathrm{B}} B / k_{\mathrm{B}} T \quad (2)$$

where m_P is the magnetic moment in units of Bohr magneton; M_{sat} is the magnetization at the saturation, and the quadratic term χ_2 accounts to the magnetic anisotropy. The optimum set of magnetic parameters is listed in Table 1. This table contains also the data referring to the human spleen (**3**, reference sample with no diagnose, Kopáni *et al*. 2015).

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Table 1. Magnetic parameters for the magnetization.

Temperature	Parameter	1, bovine spleen	2, horse spleen ferritin	3, human spleen
T = 4.6 K	M_{sat} / J.T^{-1}.kg^{-1}	0.031	0.207	
	m_p / μ_B	32	731	
	χ_1 / J.T^{-2}.kg^{-1}	0.069	0.333	
	χ_2 / J.T^{-3}.kg^{-1}	–0.0054	–0.019	
T = 2.0 K	M_{sat} / J.T^{-1}.kg^{-1}		0.262	
	m_p / μ_B		259	
	χ_1 / J.T^{-2}.kg^{-1}		0.359	
	χ_2 / J.T^{-3}.kg^{-1}		–0.023	
T = 4.6 & 2.0 K	M_{sat} / J.T^{-1}.kg^{-1}		0.248	0.856
	m_p / μ_B		340	7.26
	χ_1 / J.T^{-2}.kg^{-1}		0.338	0.098
	χ_2 / J.T^{-3}.kg^{-1}		–0.020	–0.0048

Magnetization curves for the horse spleen ferritin have been analyzed by using several models (Brem *et al.* 2006). The averaged magnetic moment of a nanoparticle m_p varies with temperature and the model employed. The model of the single Langevin function enriched by the linear susceptibility term, i.e. truncated (1), gave m_p = 350 μ_B for T = 50 K. This is not far from the data listed in Table 1. Noticeable is the fact that m_p is by an order of magnitude lower for **1** and by two orders for **3** relative to **2**.

The presence of the remnant magnetization approves a search for the full magnetic hysteresis that was successful for both, **1** and **2** (Fig. 4). The loop is more opened for **2** relative to **1**. In accordance with expectations, the hysteresis loops tend to be closed on heating for both, **1** and **2**. The characteristics of the hysteresis loops are listed in Table 2.

It is seen that on heating the remnant

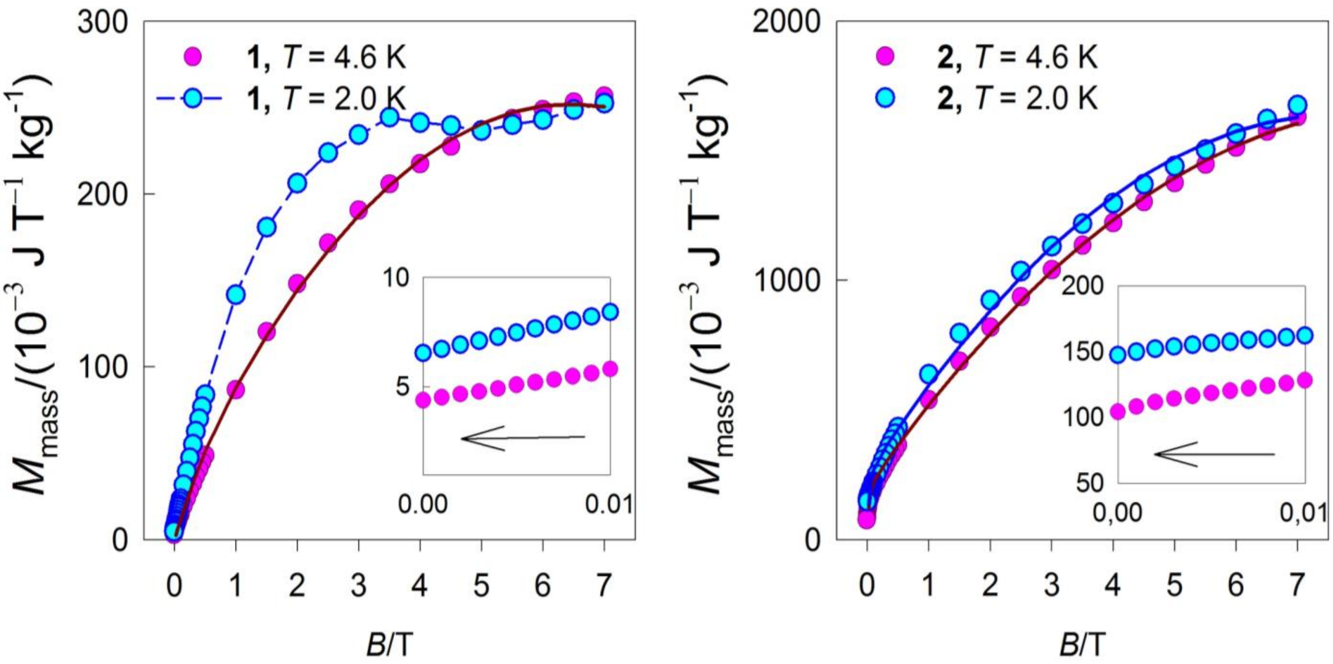

Fig. 3. Magnetization data for the bovine spleen sample **1** and horse spleen ferritin **2**. Solid lines – fitted with the extended Langevin function for T = 4.6 K. Dashed – visual guide.

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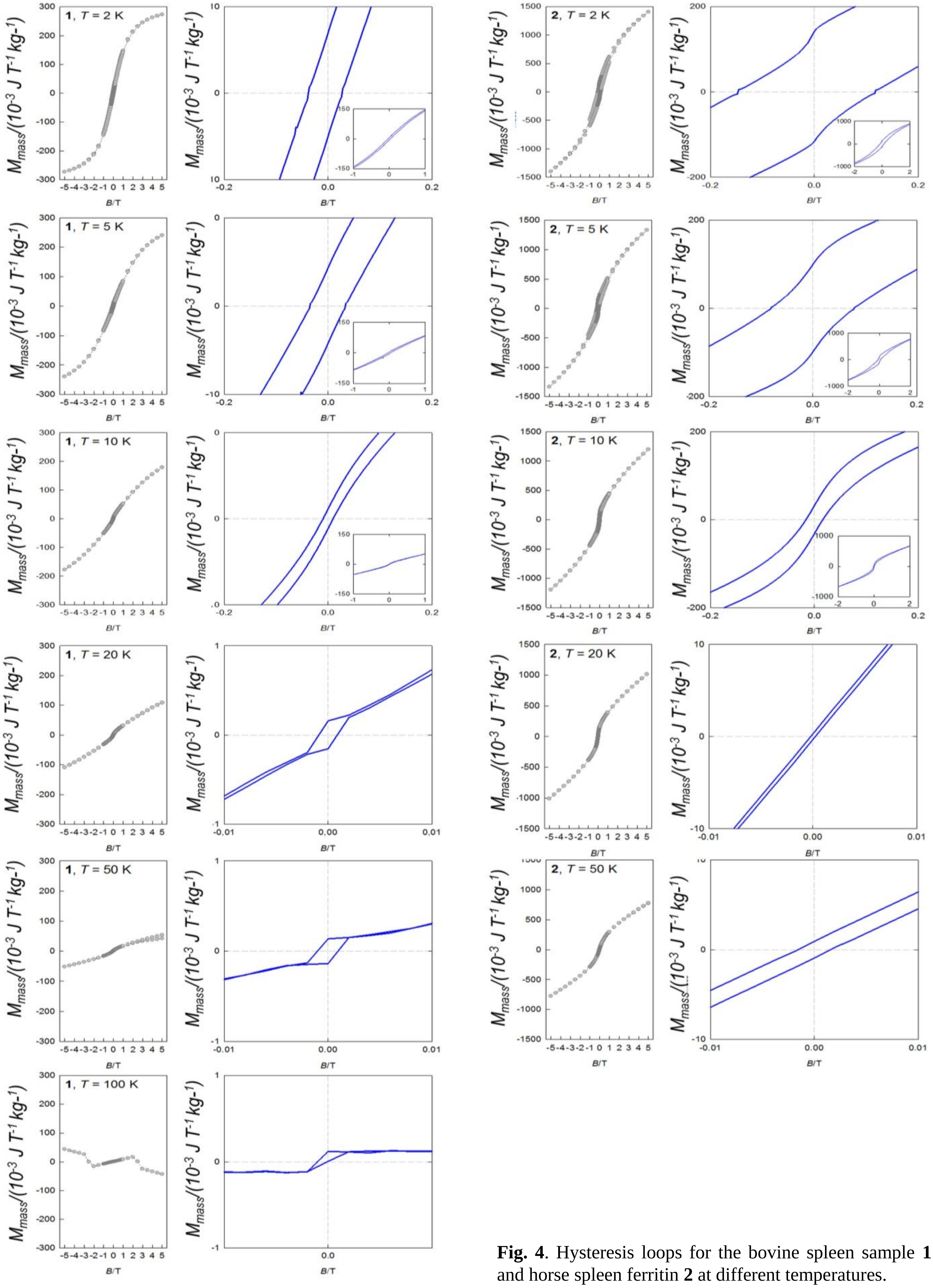

Fig. 4. Hysteresis loops for the bovine spleen sample **1** and horse spleen ferritin **2** at different temperatures.

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Table 2. Characteristics of the hysteresis loops.

***T* / K**	**1, bovine spleen**		**2, horse spleen ferritin**		**3, human spleen**	
	Remnant magnetization [a]	Coercive field *Bc* / mT	Remnant magnetization [a]	Coercive field *Bc* / mT	Remnant magnetization [a]	Coercive field *Bc* / mT
2	7.10	27.0	141.00	117.0	5.70	21.0
5	4.40	33.0	100.00	79.0 [b]	4.20	27.0
10	1.20	9.3	31.00	16.6	1.70	13.1
20	0.16	0.9	0.29	0.2	0.28	3.0
50	0.14	0.9	0.91	1.6	0.20	1.2
100	0.12	~0				

[a] M_r in units of 10^{-3} J.T^{-1}.kg^{-1} (SI); [b] B_c = 180 mT was reported by Makhlouf *et al*. 1997.

magnetization decreases progressively for both, **1** and **2** (Fig. 5). However, at T = 20 K and above, small hysteresis loop survives which points to the presence of a minor magnetically ordered phase. The development of the coercive field for **1** is more complex because on passing from T = 2 to 5 K the coercive field increased. This might be due to the presence of the above-mentioned minor phase.

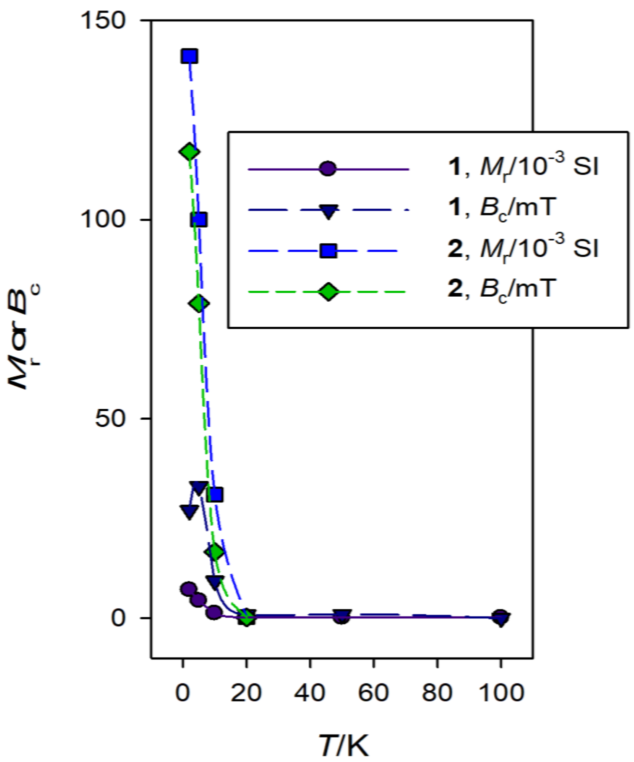

Fig. 5. Temperature evolution of the remnant magnetization and the coercive field for **1** and **2**.

In the horse-spleen ferritin **2**, the profile of the hysteresis curve adopts a wast-waisted form. This was attributed to the presence of a second ordered phase with smaller coercivity (Brem *et al*. 2006). Probably a small amount of magnetite and/or maghemite is responsible for such an effect. A comparison with the data recorded for the human spleen **3** (Kopáni *et al*. 2015) shows a great similarity to **1**: analogous values and thermal evolution of the remnant magnetization and coercive field.

Conclusions

The sample extracted from the bovine spleen possesses the magnetic response which qualitatively resembles the properties of ferritin extracted from the horse spleen. However, there exists a remarkable difference in the coercive field that is by order of magnitude higher for **2** relative to **1**. More similar properties to **1** exhibits the sample extracted from the human spleen. Also, the averaged magnetic moment per nanoparticle for **1** and **3** are much lower relative to **2**.

Acknowledgement

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Conflict of Interest

The authors declare that they have no conflict of interest.

References

Boča R, Dlháň Ľ, Kopáni M, Miglierini M, Mrázová V, Čaplovičová M (2013) Deposits of iron oxides in the human spleen. Polyhedron 66: 65-69.

Brem F, Stamm G, Hirt AM (2006) Modeling the magnetic behavior of horse spleen ferritin with a two-phase core structure. J. Appl. Phys. 99: 123906.

Bereitgestellt von Slovenská poľnohospodárska knižnica | Heruntergeladen 28.02.20 12:06 UTC

Dlháň Ľ, Kopáni M, Boča R (2019) Magnetic properties of iron oxides present in the human brain. Polyhedron 157: 505-510.

Gálvez N, Fernández B, Sánchez P, Cuest R, Ceolín M, Clemente-León M, Trasobares S, López-Haro M, Calvino JJ, Stéphan O, Domínquez-Vera J (2008) Comparative structural and chemical studies of ferritin cores with gradual removal of their iron contents. J. Am. Chem. Soc. 130: 8062.

Kirschvink JL, Kobayashi-Kirschvink A, Woodford BJ (1992) Magnetite biomineralization in the human brain. Proc. Natl. Acad. Sci. USA 89: 7683.

Kopáni M, Miglierini M, Lančok A, Dekan J, Čaplovicová M, Jakubovský J, Boča R, Mrázová H (2015) Iron oxides in human spleen. Biometals 28: 913-928.

Makhlouf SA, Parker FT, Berkowitz AE (1997) Magnetic hysteresis anomalies in ferritin. Phys. Rev. B 55: R14717.

Makohusová M, Mrázová V, Kopáni M, Boča R (2014) Magnetic deposits of iron oxides in the human brain. Nova Biotechnol. Chim. 13: 48-56.

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