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HEAT CAPACITY OF SUPERFINE OXIDES OF IRON UNDER APPLIED MAGNETIC FIELDS

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Heat capacity is one of the most characteristic and important properties when the peculiarities of magnetic nanosystems are studied. In these systems the magnetic ordering becomes obvious due to the thermal effects such as heat capacity anomalies. It was considered earlier that heat capacity change under magnetic fields applied is slight and it cannot be taken into account in thermodynamic calculations. However the experimental heat capacity data for ferrofluids under magnetic fields applied show that field and temperature heat capacity dependences have a complicated behavior and in magnetic fields an essential heat capacity change takes place. On the other hand in the literature the contradictory data about heat capacity of nanoparticles appear. According to some papers nanoparticles heat capacity can exceed heat capacity of a bulk material a few times.

Keywords: *heat capacity, hematite, maghemite, magnetite, microcalorimeter, second-order phase transition*

Experimental

The aim of the research was to study experimentally the heat capacity of magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) possessing various crystalline and magnetic structure, and which are in a colloidal state as nanoparticles and in aqua and ethanol suspensions as superfine microparticles. The research was carried out at various temperatures and under various applied magnetic fields.

Superfine magnetite was synthesized according to the procedure described [1] by means of the precipitation of Fe^{2+} and Fe^{3+} in ammonia excess [2]. The magnetite suspension obtained was repeatedly washed by distilled water up to pH=7. Ethanol-based suspension was obtained by means of repeated alcohol ablution and decantation of an aqua suspension. γ-Fe_2O_3 and α-Fe_2O_3 were obtained by means of burning superfine magnetite at 553 and 593 K, respectively, during 1 h [3]. Magnetic colloids were synthesized according to the procedure described [4]. Oleic acid and polyethylsiloxanes (PES-5, PES-V-2), transformer oil were used as surfactant and disperse media, respectively.

Heat capacity measuring was carried out by means of a microcalorimeter [5]. The research was carried out in the range of the temperatures from 283 to 253 K and under magnetic fields applied from 0 to 0.7 T. The error in the heat capacity determination was ±1.5%.

Results and discussion

Heat capacity magnitudes of nanosized magnetite and microparticle magnetite were calculated from experimental heat capacity data obtained for magnetic colloids, aqua and ethanol magnetite-based suspensions due to the fact that heat capacity of a heterogeneous system equals the sum of the component heat capacities taking into account the concentrations of the components in a system. The specific heats of the components were taken from the literature [6–8]. Specific heat of polyethylsiloxane PES-5 was experimentally determined at 298 K. The magnitude agrees with the literature data [7, 8]. Heat capacity values of microparticle magnetite for suspensions (Table 1) agree with the literature data. It should be mentioned that specific heat increases 30% for nanosized magnetite (particle size is about 10 nm) in comparison with microparticle magnetite.

Table 1 Heat capacity values for oxides in different systems

	Heat capacity/J g^{-1} K^{-1}			
	Aqua susp.	Ethanol susp.	Colloidal solution	Literature
Fe_3O_4	0.622	0.619	0.859	0.625 [9] 0.62 [10] 0.622 [11]
α-Fe_2O_3	0.59	–	–	0.65 [9] 0.652 [12]
γ-Fe_2O_3	0.608	–	–	0.679 [13] 0.679 [14]

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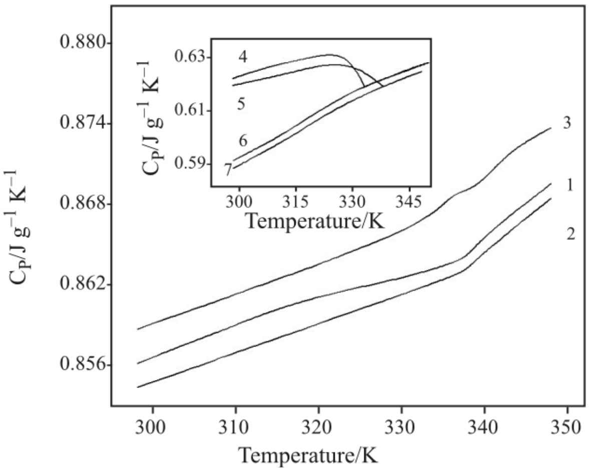

Fig. 1 Specific heat of magnetite particles as a function of temperature in zero magnetic field for: 1 – PES-5-based magnetic colloid, 2 – PES-V-2-based magnetic colloid, 3 – transformer oil-based magnetic colloid, 4 – Fe_3O_4 in aqua suspension, 5 – Fe_3O_4 in ethanol suspension, 6 – α-Fe_2O_3 in aqua suspension, 7 – α-Fe_2O_3 in ethanol suspension

Heat capacity values for oxides in different systems compared with the literature data at 298 K are represented in Table 1.

Figure 1 shows specific heat temperature dependences of magnetite for different systems. Magnetite specific heat increases for all systems (curves 1–3) with rising the temperature.

For magnetic colloids the isotherms have a small sharp curve at 338 K, i.e. slope angle of isotherms increases. Larger specific heat increase is observed. The difference between specific heat values of magnetite for colloids is about 0.5%. The curves 4, 5 (Fig. 1) correspond to the isotherms of magnetite specific heat for aqua and ethanol suspensions. Specific heat values differ within an error. In the range of the temperatures from 330 to 340 K specific heat bound is observed. This bound corresponds to transition from magnetite to hematite (curves 4, 5 coincide with curves 6, 7 for hematite).

Figures 2 and 3 show field and temperature specific heat dependences for a transition from magnetite to hematite. Specific heat of magnet is greatly changed under the applied magnetic fields (Fig. 2).

Field specific field dependences have a broad maximum which increases to 328 K (curves 1–5) with rising the temperature. Under magnetic fields more than 0.6 T specific heat values become lower than the values under a zero field. Specific heat decreasing above 0.4 T is connected with alignment of magnetic moments of domain structures. Magnetite transforms into hematite at the temperature above 328 K. In contrast to ferrimagnetic magnetite the hematite has a hexagonal crystalline structure and weak ferromagnetism. This difference results in a field dependences change. Specific heat decreases with rising the field. Visually a transition is shown in Fig. 3.

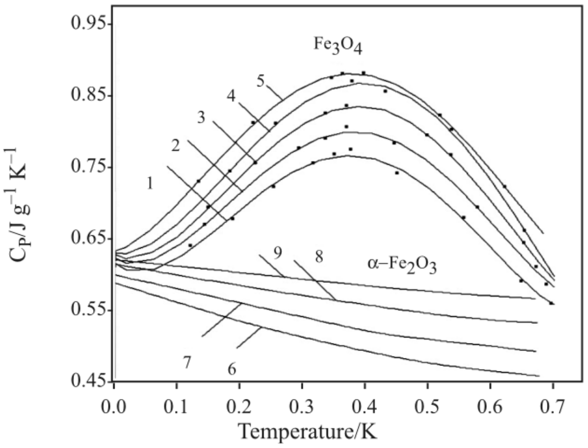

Fig. 2 Specific heat of particles of Fe_3O_4 and α-Fe_2O_3 as a function of applied magnetic field at various temperatures: 1 – 293, 2 – 298, 3 – 308, 4 – 318, 5 – 328, 6 – 298, 7 – 313, 8 – 333, 9 – 343 K

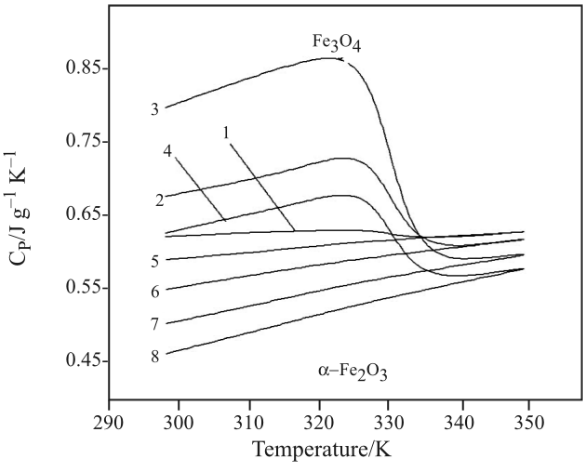

Fig. 3 Specific heat of particles of Fe_3O_4 and α-Fe_2O_3 as a function of temperature in various applied magnetic fields: 1 – 0, 2 – 0.15, 3 – 0.35, 4 – 0.65, 5 – 0, 6 – 0.15, 7 – 0.35, 8 – 0.65 T

Figure 3 shows temperature specific heat dependences for magnetite and hematite under various magnetic fields. Specific heat values for magnetite are increased to 0.4 T then sharply decrease and coincide with hematite specific heat values. Specific heat for hematite (curves 5–8) increases with rising the temperature and decreases with rising the magnetic field.

Figures 4 and 5 show field and temperature specific heat dependences for hematite and maghemite. The oxides have an identical elemental composition but differ by a crystalline lattice and by a type of the magnetism. Therefore a specific heat behavior for these oxides differs. The polytherms for

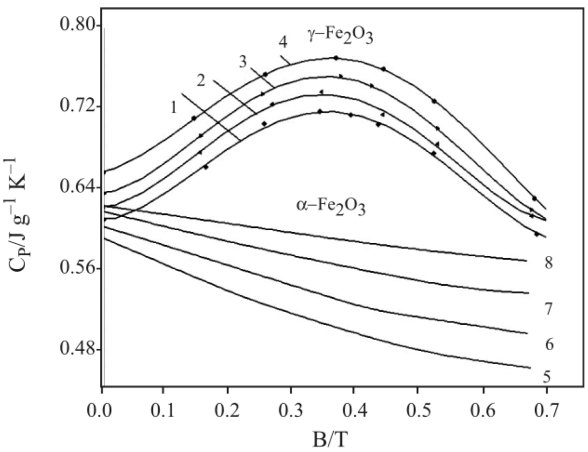

Fig. 4 Specific heat of particles of α-Fe_2O_3 and γ-Fe_2O_3 as a function of applied magnetic field at various temperatures: 1 – 298, 2 – 313, 3 – 328, 4 – 343, 5 – 298, 6 – 313, 7 – 328, 8 – 343 K

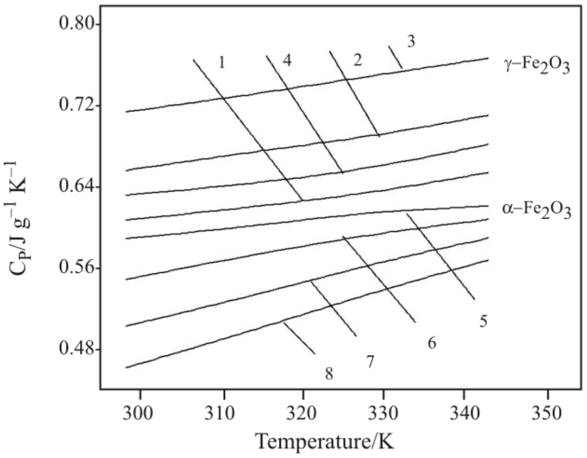

Fig. 5 Specific heat of particles of α-Fe_2O_3 and γ-Fe_2O_3 as a function of temperature in various applied magnetic fields: 1 – 0, 2 – 0.15, 3 – 0.35, 4 – 0.65, 5 – 0, 6 – 0.15, 7 – 0.35, 8 – 0.65 T

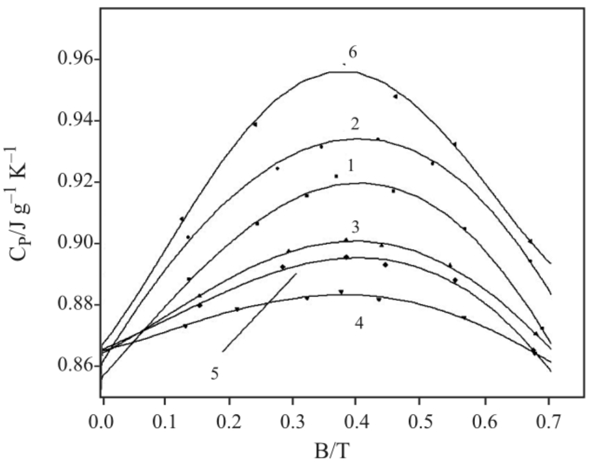

Fig. 6 Specific heat of magnetite in PES-5-based magnetic colloid as a function of applied magnetic field at various temperatures: 1 – 298, 2 – 318, 3 – 336, 4 – 338, 5 – 340, 6 – 348 K

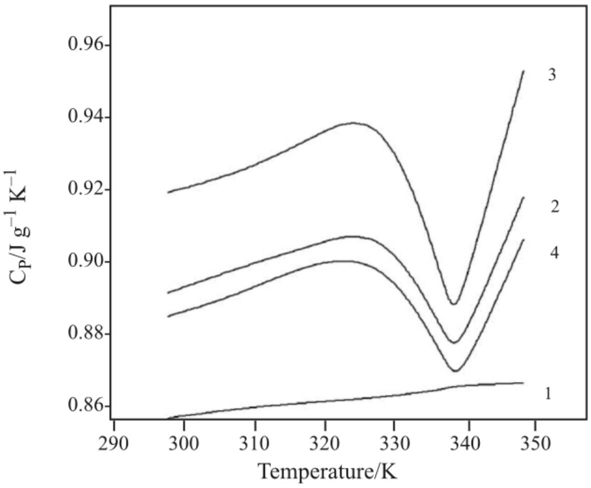

Fig. 7 Specific heat of magnetite in PES-5-based magnetic colloid as a function of temperature in various applied magnetic fields: 1 – 0, 2 – 0.15, 3 – 0.375, 4 – 0.65 T

maghemite have a broad maximum under 0.4 T (Fig. 4, curves 1–4).

Specific heat for hematite decreases with rising the magnetic field (curves 5–8). Specific heat for both oxides is linearly increased almost with rising the temperature (Fig. 5).

For hematite with rising the magnetic field the temperature influence is stronger (a slope angle of the polytherms increases). At the low temperatures the change of hematite specific heat with the magnetic field change is obvious (Fig. 5, curves 5–7).

Figures 6 and 7 show field and temperature specific heat dependences for magnetite in PES-5-based magnetic colloid. Field dependences (Fig. 6) have a broad maximum, the height of maximum increasing with rising the temperature. Then it decreases and again increases at the temperatures above 338 K.

Temperature specific heat dependences under magnetic fields are shown in Fig. 7. Specific heat has a broad maximum at 328 K and minimum at 338 K.

Such behavior of temperature magnetite dependences is characteristic for all colloids under investigation. If we compare the specific heat data for colloids with the magnetocaloric effect (MCE) data obtained by means of the same microcalorimeter we notice that at 338 K (the specific heat minimum) a sharp maximum on MCE temperature dependence takes place. Such specific heat and MCE changes are usually connected with a magnetic second-order phase transition.

Conclusions

- Specific heat of magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) being in a colloidal state as nanoparticles (~10 nm) and in aqua and ethanol suspensions as superfine microparticles (0.5–5 micron) is determined.
- Specific heat of magnetite, hematite, maghemite microparticles agrees with the literature data.
- Specific heat for magnetite in a colloidal state increases 30% in comparison with microparticle magnetite.
- On the basis of field and temperature specific heat dependences a transition of $Fe_3O_4 \rightarrow \alpha$-$Fe_2O_3$ is found in the temperature range from 330 to 340 K. A transition takes place because of oxidation process.
- Field specific heat dependences for Fe_3O_4 and γ-Fe_2O_3 have a maximum under 0.4 T. For α-Fe_2O_3 possessing parasitic ferromagnetism a specific heat decreases at all temperatures with rising the magnetic field.
- Temperature specific heat dependences has a broad maximum at 328 K and minimum at 338 K for magnetite nanoparticles, i. e. a second-order phase transition is observed.

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References

1 R. L. Carlin, Magnetochemistry, Springer, New York 1986.
2 V. V. Korolev, A. E. Zavadskii, V. I. Yashkova, O. V. Balmasova, K. N. Zheleznov and A. G. Ramazanova, Dokl. Akad. Nauk., 361 (1998) 362.
3 E. P. Kotov and M. I. Rudenko, Tapes and Disks in devices for magnetic recording, Moscow 1986, p. 224 (in Russian).
4 L. A. Shmeleva, L. N. Savina, N. I. Dyupovkin and V. V. Korolev, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 38 (1995) 71.
5 V. V. Korolev, A. S. Romanov and I. M. Arefyev, Zh. Fiz. Khim., 80 (2006) 380.
6 R. Sobbah, A. Xu-Wu, J. S. Chickos, M. L. Planas Leitao, M. V. Roux and L. A. Torres, Thermochim. Acta, 331 (1999) 93.
7 V. E. Fertman, Ferrofluids, Minsk 1988, p. 184 (in Russian).
8 I. I. Skorohodov, Physical-Chemical and Operation Properties of Polyethylsiloxanes, Moscow 1978, (in Russian).
9 J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc., 73 (1951) 3891.
10 S. A. Zonis and G. A. Simonov, Hand-book of Chemist, 1963, p. 741–744 (in Russian).
11 I. K. Kikoin, Tables of Physical Values, Hand-book, Moscow 1976, p. 1008 (in Russian).
12 F. Gronvold, E. F. Westrum and C. Chien, J. Chem. Phys., 30 (1959) 528.
13 V. A. Rabinovich and Z. Ya. Havin, Brief Chemical Hand-book, 1977, p. 63.
14 G. K. Demenskii, Dissertation Thesis, Moscow State University, 1977.

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