INTRODUCTION

Strong interactions of the electronic and spin subsystems with crystal lattices are observed in some magnets, which results in anomalies of their magnetic, electric, optical, magnetooptical, and elastic properties [1]. In this respect, the giant magnetocaloric effect and magnetostriction [1] and giant magnetoresistance [2] observed in magnets close to the Curie temperature ($T_C$) are of great interest for theory and practical applications. The magnetocaloric effect in rare-earth metal manganites, in particular, nanoscale manganites, remains virtually unstudied. It can be comparable with that in gadolinium, which makes the magnetocaloric substances specified promising materials for refrigerator devices, medicine (hyperthermia of malignant tumors), and other nanotechnologies. On the other hand, it was established experimentally that the Curie temperature of nanoscale materials differs considerably from the Curie temperature of bulk materials. The search for nanoscale materials that have large values of the effects specified at room temperatures and in weak magnetic fields is therefore the problem of great current interest.

In this work, we present the results of an experimental study of the magnetocaloric effect and specific heat capacity of an aqueous suspension of samarium ferrite. Thanks to such thermal effects as heat capacity anomaly [1], the existence of magnetic ordering in such systems becomes obvious. It was assumed earlier [2] that field-induced changes in heat capacity were insignificant and could be ignored in thermodynamic calculations. Our experimental data on the heat capacity of an aqueous suspension of samarium ferrite in magnetic fields, however, show that, for instance, calculations of the magnetic entropy component require the magnetic heat capacity component to be known.

EXPERIMENTAL

Measurements of the magnetocaloric effect and specific heat capacity of an aqueous suspension of samarium ferrite were taken on an automated microcalorimetric unit [3], which was an isothermal-shell microcalorimeter. The measuring cell with an isothermal shell was placed into a gap between the poles of an electromagnet (60 mm). This allowed us to measure magnetocaloric effect and specific heat capacity in magnetic fields of from 0 to 0.7 T over the temperature range 288–343 K.

The heat capacity was calculated using the equation

$$C_p = \frac{Q}{\Delta T} - W,$$

where $Q$ is the amount of heat released in the calorimeter, $\Delta T$ is the change in temperature in the main calorimetric experiment period corrected for heat exchange at the initial and final stages, and $W$ is the calorimeter constant. The sensitivity of the unit was $2 \times 10^{-5}$ K, the accuracy of magnetocaloric effect measurements was $\pm 0.1\%$, and the accuracy of heat capacity measurements was $\pm 1\%$.

Samarium ferrite SmFeO$_3 \cdot$ FeO was synthesized by the coprecipitation of iron(II, III) and samarium salts taken in stoichiometric amounts with excess alkali at 353 K. The product was black, and its suspension strongly reacted to magnetic fields. The suspension of samarium ferrite was repeatedly washed with distilled water to pH 7. Eventually, the degree of washing from sulfate, chloride, and nitrate ions was checked by
measuring the conductivity of washes. Washing was considered complete when conductivity decreased to 1.77 $\mu$S cm$^{-1}$. The size of samarium ferrite nanoparticles (3–5 nm on average) was determined by the X-ray diffraction method. Samarium ferrite particles were in the aggregated state in the aqueous suspension. The size of major fraction aggregates determined microscopically was 10–50 $\mu$m. Aggregates were round-shaped and dark brown in transmission. The content of samarium ferrite in aqueous suspension samples for calorimetric measurements was 61 wt %.

RESULTS AND DISCUSSION

Magnetic field switching on increased the temperature of the aqueous suspension of samarium ferrite; that is, a positive magnetocaloric effect was observed. When the field was switched off, the temperature decreased (a negative magnetocaloric effect). Below, the data on the positive magnetocaloric effect are given.

The field dependences of the magnetocaloric effect (Fig. 1) show that, at all temperatures, this effect increased nonlinearly in fields of from 0 to 0.7 T as the magnetic field induction grew. The temperature dependences of the magnetocaloric effect in various magnetic fields are shown in Fig. 2. The magnetocaloric effect value for the aqueous solution of samarium ferrite increased sharply at 300–320 K and reached a maximum at the same temperature (313 K) in all magnetic fields. The height of the maximum increased as the magnetic field grew and reached a maximum (0.077 K) at 0.6 T. The presence of a maximum in this temperature range for the system containing samarium ferrite particles is related to the second-order magnetic phase transition.

The magnetic field and temperature dependences of the specific heat capacity of the aqueous suspension of samarium ferrite are shown in Figs. 3 and 4, respectively. The specific heat capacity isotherms have maxima in fields of 0.4 T at all temperatures (Fig. 3). The temperature dependence of the specific heat capacity is complex in character. In zero field, the heat capacity increases linearly (Fig. 4, curve 1). In magnetic fields, the heat capacity has a maximum at 298 K and a minimum at 313 K. The maximum first increases as the magnetic field induction grows to 0.375 T and then decreases. The temperature of the heat capacity maximum coincides with the temperature of the magnetocaloric effect minimum (300 K), and the temperature of the heat capacity minimum, with the temperature of magnetocaloric effect maximum (313 K). This does not contradict the well-known thermodynamic equation

$$\Delta T = T/C_m(\partial I/\partial T)\Delta H,$$

where the magnetocaloric effect ($\Delta T$) and the heat capacity of a magnet ($C_m$) are inversely proportional to each other and $\partial I/\partial T$ is the derivative of magnetization with respect to temperature. At the temperature of the magnetocaloric effect maximum, the specific heat...