Heat capacity peculiarities of hard magnetic materials of Nd-Fe-B and Sm-Co systems

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Abstract. The articles presents new experimental data on the heat capacity of hard magnetic materials of brands N35M, N35H, N35SH, as well as YX18, YX24 and YXG22, YXG30 with main components represented by the crystalline phases of Nd$_2$Fe$_{14}$B, SmCo$_5$ and Sm$_2$Co$_{17}$ type, respectively. The temperature range from 190 to 800…1270 K has been investigated by the method of differential scanning calorimetry with an error of 2–3%. The approximation dependences of specific heat coefficient have been obtained. The character of changes of the heat capacity in the region of the Curie point has been specified, and its critical indices and critical amplitudes have been defined.

1. Introduction
A large number of experimental studies are devoted to measuring the thermophysical properties of substances in a magnetic field. It is known that under its influence some interesting thermal effects are observed in the magnetic materials. In particular there are magnetostrictive and magnetocaloric effects. Alloys based on rare-earth metals (REM), including REM alloys with 3d-transition metals, are one of the most interesting and promising classes of magnetic materials. Modern permanent magnets based on Nd-Fe-B and Sm-Co compounds, which have to date the highest characteristics, such as coercive force, residual magnetic induction and maximum magnetic product, have been investigated. Literature search has revealed that the magnetic properties of Nd-Fe-B and Sm-Co compounds were studied in sufficient detail. However, it was noticed that there are practically no reliable data on the thermophysical properties of such magnets, in particular, on the heat capacity. It was possible to find two papers [1, 2] in which the results of heat capacity measurements of compounds based on SmCo$_5$ were given, but they were obtained in very narrow temperature intervals. A sparse data on the caloric properties of compounds of the Nd-Fe-B system are qualitative in nature. In this regard the aim of the present work was to measure the specific heat capacity of some technically important compounds of Nd-Fe-B and Sm-Co systems in a wide temperature range of a solid state, including the region of the magnetic phase transition, as well as to clarify the question about the influence of the residual magnetization on the heat capacity.

2. Experimental technique
The specific heat coefficient ($C_P$) was investigated by the method of differential scanning calorimetry (DSC) using the automated experimental setup DSC 404 F1 [3] produced by the German company NETZSCH. Measurements were carried out in low (190–375 K) and high temperature (318–800…1270 K) ranges with a heating rate of 2 K/min and 5 K/min, respectively, in flowing argon.
atmosphere (20 ml/min). The purity of argon was 99.998 vol. %. The control measurements of mass and magnetic field generated by the sample were carried out directly before and after the experiments. The analytical balances AND GH-252 [4] and the magnetometer Aktakom ATE-8702 [5] were used for these measurements. The working volume of the unit was evacuated to a vacuum of 1 Pa and several times washed with argon before the experiments. The used calibration samples were sapphire – for the low temperature range and 12Kh18N10T stainless steel – for the high temperature range. All the investigated samples of magnets were placed in platinum crucibles. It was taken into account that the sample should not interact with the material of the measuring cell and protective gas atmosphere when choosing the crucible material. The estimated error of the obtained data, confirmed by experiments with reference samples of sapphire and platinum, was 2–3%.

Experiments were carried out on samples of hard magnetic materials of brands N35M, N35H, N35SH, as well as YX18, YX24 and YXG22, YXG30 containing the crystalline phases of Nd\(_2\)Fe\(_{14}\)B, SmCo\(_5\) and Sm\(_2\)Co\(_{17}\) type, respectively, as a main component. The technology of their manufacture is described in [6] and their technical characteristics are listed in [7, 8]. According to the information provided by the manufacturer the samples of magnets based on Nd-Fe-B compounds have the following chemical structure, namely Fe ~ 71%, Nd ~ 24–27%, Dy ~ 0.5–2.5%, Co ~ 1% and B ~ 1%. According to the composition various brands differ in the content of dysprosium, which is 0.5, 1 and 2.5% for brands N35M, N35H and N35SH, respectively. From the viewpoint of the known properties, the specimens of different grades differ in the range of operating temperatures and the value of the coercive force. For the studied compounds we have that the more dysprosium is in the sample, the higher the coercive force and the upper limit of the permitted temperature interval are. For the magnets of Sm-Co system according to the manufacturer's data [8] the samples of various brands differ in the value of the maximum magnetic product, and from the point of view of chemistry the differences are due to small additions of Pr, Fe, Cu and Zr. The specimens had the shape of cylinders 1.5–2 mm long and 5 mm diameter with plane base for better thermal contact with the bottom of the crucible.

3. Procedure of the experiments and data processing

Initially experiments to determine the temperature dependence of the residual magnetization and to find the maximum working temperature \(T_{max}\) were performed for the samples of each brand. The maximum working temperature was selected for the irreversible change of residual magnetization not to occur after heating to this temperature and subsequent cooling down to 293 K. The experiments consisted of successive cycles of heating at a rate of 5 K/min, isothermal interval for 30 minutes and cooling at a rate of 5 K/min of the initially magnetized sample in the furnace of DSC 404 F1 calorimeter. The maximum heating temperature was increased for each subsequent cycle, and the magnetic field of the sample was measured in gaps between cycles. Before the experiments the magnetic field on the surface of the samples was 250 mT and 100 mT for Nd-Fe-B and Sm-Co systems, respectively.

At the next stage, \(C_p\) measurements of investigated brands of magnetic samples were carried out in two temperature intervals. At first, a series of experiments in the low temperature range (190–375 K) realized for magnetized samples. Then a series of experiments in the high temperature range (318–800…1270 K) was performed for complete demagnetizing of the samples at heating above the Curie temperature \(T_C\). After that, the experiments were performed in all the investigated temperature intervals with fully demagnetized samples.

The complex behavior of the temperature dependence of \(C_p\) did not allow obtaining a single approximation equation. Therefore, the whole measurement interval was divided into regions, in which separate data processing was carried out. In the subcritical region of a monotonic change of \(C_p\) the primary data were approximated by the method of least squares by polynomials of the following form:

\[
C_p(T) = \sum_{i=0}^{n} A_i T^i.
\]
In the field of magnetic phase transition the results were described using the scaling theory [9]. From the values of $C_p(T)$, we separated the magnetic contribution for this purpose:

$$C_{P_{mag}}(T) = C_p(T) - C_{P_{para}}(T),$$  \hspace{1cm} (2)

where $C_{P_{para}}(T)$ was found by the linear approximation of experimental data in the region of paramagnetic state. The magnetic component of $C_p$ was written in the form:

$$C_{P_{mag}} = A|\tau|^\alpha + B,$$

\hspace{1cm} (3)

where $A, B$ are the constants, $\tau = (T - T_C)/T_C$ is the reduced temperature, and $\alpha$ is the critical exponent of specific heat capacity. It is obvious that $B = C_{P_{mag}}(T_C)$. Then, introducing a new variable $Y_{mag} = C_{P_{mag}} - C_{P_{mag}}(T_C)$, we obtain from (3):

$$\ln(Y_{mag}) = \ln(A) + \alpha \ln(|\tau|).$$

\hspace{1cm} (4)

As it is seen from (4), when performing the linear approximation of $\ln(Y_{mag})$ by $\ln(|\tau|)$ it is possible to calculate the values of the critical amplitude $A$ and the critical exponent $\alpha$.

4. Results and discussion

The experiments to determine the maximum working temperature showed full agreement of this parameter with values declared by the manufacturer [7, 8] only for brands N35H and N35SH. For other brands of magnets $T_{max}$ was higher than the manufacturer's values by 10-30 K. According to the results of our measurements $T_{max}$ for brands N35M, N35H, N35SH, as well as YX18, YX24 and YXG22, YXG30 were 388, 393, 423 K, and 533, 544 K and 584, 554 K, respectively.

The measurements have shown that the magnetic phase transition in the form of sharp maximum was distinctly manifested in the temperature dependence of $C_p$ in the high temperature region. According to the obtained experimental data the Curie temperature for magnets of brands N35M, N35H, N35SH, as well as YX18, YX24 and YXG22, YXG30 were 591, 573, 581 K, and 959, 949 K and 1067, 1063 K, respectively. The experimental results for specific heat of magnet of brand N35H in a magnetized and demagnetized state are shown in figure 1. It can be seen that the curves of the second and third heating lie 2% higher compared with the curve of the first heating starting from a temperature of 420 K. Apparently, this is caused by the demagnetization process of the sample occurring in the first heating, wherein the sample is completely demagnetized by heating above the region of the magnetic phase transition. Two subsequent heating cycles were performed for already demagnetized sample. The differences between the first and subsequent heating on polytherms of heat capacity can also be caused by the abatement of thermal stresses, the release of sorbed substances and other processes that are typical for high temperature annealing. Nevertheless, the data on $C_p$ obtained in all thermal cycles are reproduced among themselves within the limits of the estimated measurement errors. A similar situation is typical for experiments with samples of other brands of magnets that we have investigated. Thus it can be concluded, that either the heat capacity is completely independent of the residual magnetization, or this dependence is too weak to be reliably fixed by our instruments. Small systematic differences of studied properties for magnetized and demagnetized samples support the second assumption. However, the magnitude of these deviations is lower or at the level of the measurement error.

The recommended $C_p$ data for all grades of the magnetic systems studied in this work are shown in figure 2. The temperature dependences of $C_p$ for magnets of Nd-Fe-B system are very close to each other. Hence it can be concluded, that small additions of dysprosium have little effect on $C_p$. The only noticeable difference for samples of different brands was $T_C$ shift by a few degrees. Substantial differences (>20%) in $C_p$ of alloys based on SmCo$_5$, which are observed in the region of monotonous change of properties, invoke some questions. According to the manufacturer, the chemical composition of these brands (YX18 and YX24) is almost identical and differs by small impurities.
which cannot lead to such significant deviations. Apparently, the differences in $C_p$ are associated with the samples production technology. The results of $C_p$ measurements of compounds based on SmCo$_5$, that were obtained in earlier papers [1, 2], are also presented in figure 2 for comparison. As can be seen published data are in satisfactory agreement with our results.

**Figure 1.** Heat capacity of Nd-Fe-B magnet of brand N35H: 1 – 1-st heating, 2 – 2-nd heating, 3 – 3-rd heating.

**Figure 2.** Comparison of the heat capacity experimental results: 1 – N35M, 2 – N35H, 3 – N35SH, 4 – YX18, 5 – YX24, 6 – YXG22, 7 – YXG30, 8 – [1], 9 – [2].

It is impossible to describe the dependence of $C_p(T)$ on a single relation. Therefore, the entire measurement interval was divided into areas in which the separate data processing was carried out. Outside the temperature intervals directly adjoined to the Curie point the primary data were approximated by the method of least squares by polynomial dependences. The approximations were made using scaling dependences for the magnetic phase transition area. Approximation dependences of specific heat are given in the table. It was found that the critical indices for ferromagnetic and paramagnetic areas differed significantly.
### Table. Approximations of specific heat capacity of hard magnetic materials of brands N35M, N35H, N35SH, YX18, YX24, YXG22 and YXG30.

| Temperature interval, K | Approximation equation of $C_p(T)$, J(g K)$^{-1}$ | Standard deviation, % |
|-------------------------|-----------------------------------------------|----------------------|
| **N35M**                |                                               |                      |
| 190 – 565               | $0.239 + 1.64 \times 10^{-4} T + 5.98 \times 10^{-7} T^2$ | 0.44                 |
| 565 – 591.1             | $0.389 + 5.73 \times 10^{-3} T + 6.36 \times 10^{-2} ((591.1 - T)/591.1)^{0.19}$ | 0.72                 |
| 591.1 – 625             | $0.389 + 5.73 \times 10^{-3} T + 0.11 \times 10^{-2} ((T - 591.1)/591.1)^{1.06}$ | 1.49                 |
| 625 – 670               | $0.462 - 0.406 ((T - 591.1)/591.1) + 1.137 ((T - 591.1)/591.1)^2$ | 0.06                 |
| 670 – 800               | $0.389 + 5.73 \times 10^{-3} T$ | 0.22                 |
| **N35H**                |                                               |                      |
| 190 – 550               | $0.287 - 5.34 \times 10^{-5} T + 8.87 \times 10^{-7} T^2$ | 0.34                 |
| 550 – 573.3             | $0.357 + 1.15 \times 10^{-3} T + 6.34 \times 10^{-2} ((573.3 - T)/573.3)^{0.18}$ | 0.30                 |
| 573.3 – 600             | $0.357 + 1.15 \times 10^{-3} T + 0.14 \times 10^{-2} ((T - 573.3)/573.3)^{0.99}$ | 1.58                 |
| 600 – 680               | $0.464 - 0.374 ((T - 573.3)/573.3) + 1.196 ((T - 573.3)/573.3)^2$ | 0.09                 |
| 680 – 800               | $0.357 + 1.15 \times 10^{-3} T$ | 0.26                 |
| **N35SH**               |                                               |                      |
| 190 – 550               | $0.227 + 2.31 \times 10^{-4} T + 5.49 \times 10^{-7} T^2$ | 0.43                 |
| 550 – 580.7             | $0.360 + 1.13 \times 10^{-3} T + 6.22 \times 10^{-2} ((580.7 - T)/580.7)^{0.18}$ | 0.59                 |
| 580.7 – 610             | $0.360 + 1.13 \times 10^{-3} T + 0.13 \times 10^{-2} ((T - 580.7)/580.7)^{0.99}$ | 1.50                 |
| 610 – 660               | $0.471 - 0.504 ((T - 580.7)/580.7) + 1.943 ((T - 580.7)/580.7)^2$ | 0.07                 |
| 660 – 800               | $0.360 + 1.13 \times 10^{-3} T$ | 0.23                 |
| **YX18**                |                                               |                      |
| 190 – 940               | $0.279 + 2.87 \times 10^{-4} T - 4.47 \times 10^{-5} T^2$ | 1.13                 |
| 940 – 959.2             | $0.459 - 4.23 \times 10^{-3} T + 5.18 \times 10^{-2} ((959.2 - T)/959.2)^{0.19}$ | 0.43                 |
| 959.2 – 970             | $0.459 - 4.23 \times 10^{-3} T + 0.34 \times 10^{-5} ((T - 959.2)/959.2)^{1.57}$ | 0.98                 |
| 970 – 1010              | $0.465 - 2.214 ((T - 959.2)/959.2) + 27.374 ((T - 959.2)/959.2)^2$ | 0.45                 |
| 1010 – 1270             | $0.459 - 4.23 \times 10^{-3} T$ | 0.59                 |
| **YX24**                |                                               |                      |
| 190 – 920               | $0.280 + 1.59 \times 10^{-4} T - 1.79 \times 10^{-5} T^2$ | 0.87                 |
| 920 – 948.9             | $0.362 - 4.93 \times 10^{-3} T + 5.83 \times 10^{-5} ((948.9 - T)/948.9)^{0.18}$ | 0.25                 |
| 948.9 – 975             | $0.362 - 4.93 \times 10^{-3} T + 0.19 \times 10^{-5} ((T - 948.9)/948.9)^{0.79}$ | 0.26                 |
| 975 – 1020              | $0.354 - 0.442 ((T - 948.9)/948.9) - 0.737 ((T - 948.9)/948.9)^2$ | 0.39                 |
| 1020 – 1270             | $0.362 - 4.93 \times 10^{-3} T$ | 1.12                 |
| **YXG22**               |                                               |                      |
| 190 – 1040              | $0.287 + 2.09 \times 10^{-4} T + 6.28 \times 10^{-5} T^2$ | 1.48                 |
| 1040 – 1058             | $0.627 - 8.87 \times 10^{-5} T + 2.42 \times 10^{-5} ((1067.4 - T)/1067.4)^{0.29}$ | 0.28                 |
| 1058 – 1067.4           | $0.627 - 8.87 \times 10^{-5} T + 6.44 \times 10^{-5} ((1067.4 - T)/1067.4)^{0.06}$ | 0.16                 |
| 1067.4 – 1090           | $0.627 - 8.87 \times 10^{-5} T + 1.66 \times 10^{-5} ((T - 1067.4)/1067.4)^{1.38}$ | 0.83                 |
| 1090 – 1115             | $0.581 - 1.12 ((T - 1067.4)/1067.4) - 1.358 ((T - 1067.4)/1067.4)^2$ | 0.08                 |
| 1115 – 1270             | $0.627 - 8.87 \times 10^{-5} T$ | 0.50                 |
| **YXG30**               |                                               |                      |
| 190 – 1045              | $0.320 + 1.42 \times 10^{-4} T + 1.29 \times 10^{-7} T^2$ | 1.47                 |
| 1045 – 1055             | $0.575 - 2.46 \times 10^{-3} T + 2.29 \times 10^{-5} ((1063 - T)/1063)^{0.33}$ | 0.21                 |
| 1055 – 1063             | $0.575 - 2.46 \times 10^{-3} T + 7.21 \times 10^{-5} ((1063 - T)/1063)^{0.08}$ | 0.13                 |
| 1063 – 1084             | $0.575 - 2.46 \times 10^{-3} T + 0.78 \times 10^{-5} ((T - 1063)/1063)^{1.54}$ | 0.99                 |
| 1084 – 1115             | $0.610 - 2.53 ((T - 1063)/1063) + 27.825 ((T - 1063)/1063)^2$ | 0.15                 |
| 1115 – 1270             | $0.575 - 2.46 \times 10^{-3} T$ | 0.38                 |
5. Conclusion
For the first time, it has become possible to obtain new experimental data on specific heat of hard magnetic materials of brands N35M, N35H, N35SH, as well as YX18, YX24 and YXG22, YXG30 containing the crystalline phases of Nd$_2$Fe$_{14}$B, SmCo$_5$ and Sm$_2$Co$_{17}$ type, respectively, as a main component. The measurements were carried out by the method of differential scanning calorimetry with an error of 2–3% in the temperature range from 190 to 800…1270 K. The approximation dependences of specific heat coefficient have been obtained. The character of changes of the heat capacity in the region of the Curie point has been specified. It has been shown that the critical indices for the ferromagnetic and paramagnetic regions vary significantly. The values of the maximum working temperature of the permanent magnets created from the investigated ferromagnets have been determined. It was shown that the presence of the constant magnetic field did not lead to noticeable changes in the heat capacity of investigated materials.

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