Negative Thermal Expansion and Spontaneous Magnetostriction of $Nd_2Fe_{16.5}Cr_{0.5}$ Compound *

Li-Yu HAO(郝立宇)[1], Tie Yang(杨铁)[1**], Ming Tan(谭明)[2**]
[1] School of Physics Science and Technology, Southwest University, Chongqing 400715
[2] College of Science, Henan Agricultural University, Zhengzhou 450002

(Received 24 September 2019)

The structural, thermal expansion, and magnetic properties of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound are investigated by means of x-ray diffraction and magnetization measurements. The $Nd_2Fe_{16.5}Cr_{0.5}$ compound has a rhombohedral Th_2Zn_{17}-type structure. There exists a small negative thermal expansion resulting from a spontaneous magnetostriction in the magnetic state of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound. The average thermal expansion coefficient is -1.06×10^{-6}/K in a temperature range 299–394 K. The spontaneous magnetostrictive deformation and the Curie temperature are discussed.

PACS: 65.60.+a, 75.80.+q, 75.30.Et, 75.60.Ej DOI: 10.1088/0256-307X/37/1/016501

Materials with negative thermal expansion (NTE) coefficients and their composites with other materials are used in electric and optical devices as well as structural materials under high thermo-mechanical load to achieve a desired overall thermal expansion coefficient. Unfortunately, the only known materials with NTE coefficients are several oxide systems such as ZrW_2O_8 and HfW_2O_8, and a few Invar alloys.[1−5] Discovery of new materials with NTE coefficients and further understanding of the NTE mechanism may, therefore, play an important role in applications and theory. In the recent decades,[6−9] it was found that there was NTE in rare earth transition metal compounds with Th_2Ni_{17}-type structure or with Th_2Zn_{17}-type structure. It is very interesting to discovery the NTE of the $Gd_2Fe_{16}Cr$ compound in a wide temperature range from 292 to about 572 K.[10] Another interesting result is the presence of near-zero expansion in the $Nd_2AlFe_{15}Cr$ compound near room temperature.[11] This makes it necessary to further investigate the thermal expansion behaviors of other rare earth transition metal compounds with both the Th_2Ni_{17}-type structure and Th_2Zn_{17}-type structure.

In this work, the thermal expansion behavior and its spontaneous magnetostrictions of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound are investigated by x-ray dilatometry and magnetization measurements.

The raw materials of Nd, Fe, and Cr used in the experiment were at least 99.98% purity. The compound of $Nd_2Fe_{16.5}Cr_{0.5}$ was prepared by arc melting in an argon atmosphere of high purity. The ingot was re-melted four times to ensure its homogeneity and sealed in an evacuated silica vacuum tube, then annealed at 1050℃ for 5 days, after that, quenched in water. The ingot of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound was ground into powder. To decrease the stress, the powder of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound was sealed in a silicon vacuum tube, annealed at 300℃ for 3 h and slowly cooled to room temperature. The powder x-ray diffraction with Cu K_α radiation was used to examine the phase structure of the sample of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound. The Curie temperature T_c was derived from the temperature dependence of the magnetization curve measured by a vibrating sample magnetometer (VSM) in a field 40 kA/m. The thermal expansion of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound was measured by x-ray dilatometry. For the determination of the lattice parameters a and c of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound in the temperature range from 299 to 619 K, the powder sample was placed into an evacuated high-temperature chamber and step scanning (in steps of 0.01°) x-ray diffraction patterns of the (113) and (303) reflections were recorded by the x-ray diffractometer with Cu K_α radiation monochromatized by a single-crystal graphite monochromator. The experimental error in the determination of a and c was 10^{-4} nm. The magnetostrictive deformations λ_a, λ_c, and ω_s were determined by the differences between the experimental values a_m, c_m, and v_m of the lattice parameters at a given temperature and the corresponding values a_p, c_p, and v_p extrapolated from the paramagnetic range according to the Debye theory and the Grüuneisen relation. The Debye temperature 400 K of R_2Fe_{17} compound (where R is rare earth elements) was used to extrapolate the temperature dependence of the lattice parameters of the sample, as it was carried out in the literature.[6−11]

The XRD pattern of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample at room temperature is shown in Fig. 1. The indices of crystallographic plane (hkl) of reflections are marked on the peaks correspondingly. It is indicated that the $Nd_2Fe_{16.5}Cr_{0.5}$ compound is in a single phase with a rhombohedral Th_2Zn_{17}-type structure (space group, $R\bar{3}m$). The lattice parameters a and c are 0.85754 nm

*Supported by the National Natural Science Foundation of China under Grant Nos 50871074 and 61474082, the Henan Agricultural University Start-up under Grant No 20190703Y00005.
**Corresponding author. Email: tanming912@163.com; yangtie@swu.edu.cn

and 1.24732 nm, respectively, and the unit-cell volume v is 0.7944 nm^3.

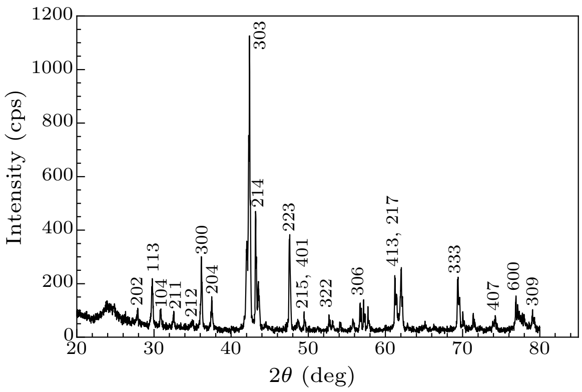

Fig. 1. The x-ray diffraction pattern of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound at room temperature (about 300 K).

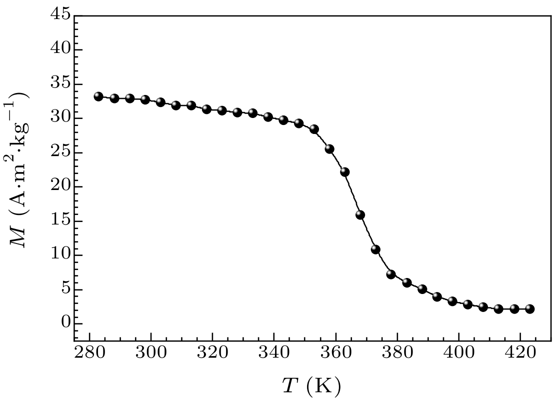

Fig. 2. Temperature dependence of the magnetization of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound in a field of 40 kA/m.

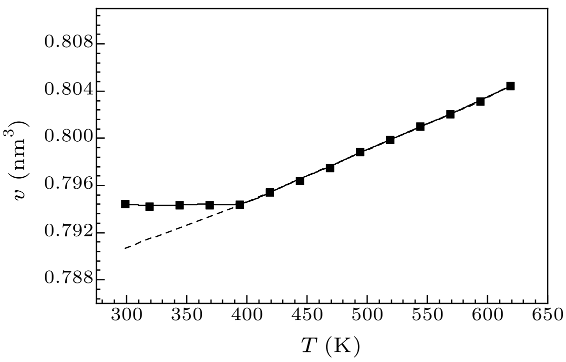

Fig. 3. Temperature dependence of the unit cell volume v of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound. The dashed line represents the values extrapolated from the paramagnetic range.

The temperature dependence of magnetization of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample is shown in Fig. 2. It is obvious that only one magnetic phase exists in the sample. This is different from the $Nd_2Fe_{14.5}Cr_{2.5}$ compound,[12] in which there are two magnetic phases. From Fig. 2, one can estimate the Curie temperature of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound to be about 375 K. This value is about 45 K higher than that of the mother compound Nd_2Fe_{17}.[13] Just as the $Gd_2Fe_{16}Cr$ compound,[10] this may be attributed to the fact that Cr atoms prefer to occupy the 6c sites of the Th_2Zn_{17}-type structure.

The x-ray diffraction of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample shows that the sample is still in a single phase with the rhombohedral Th_2Zn_{17}-type structure from 299 to 619 K. Figure 3 shows the temperature dependence of unit-cell volume v of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample. It is obvious that there is a small negative volume thermal expansion of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample in the temperature 299–394 K.

If the variation of the rate of v is considered from 299 K to 619 K. One can obtain the average thermal expansion coefficients $\bar{\alpha} = \frac{\Delta v}{\Delta T \bar{v}} = -1.06 \times 10^{-6}$/K in the temperature range 299–394 K, and 5.61×10^{-5}/K in the temperature range 394–619 K, respectively. It is interesting that the absolute value of $\bar{\alpha}$ in the temperature range 299–394 K is very small to be near zero. This small thermal expansion coefficient was also found in the $Nd_2AlFe_{15}Mn$ compound below 340 K.[11] Just as in the $Nd_2AlFe_{15}Mn$,[11] $Tb_2Fe_{16}Cr$[14] and $Gd_2Fe_{16}Cr$ compounds,[10] this anomalous thermal expansion in the temperature range 299–394 K is ascribed to the existences of strong magneto-volume effect in the $Nd_2Fe_{16.5}Cr_{0.5}$ compound.

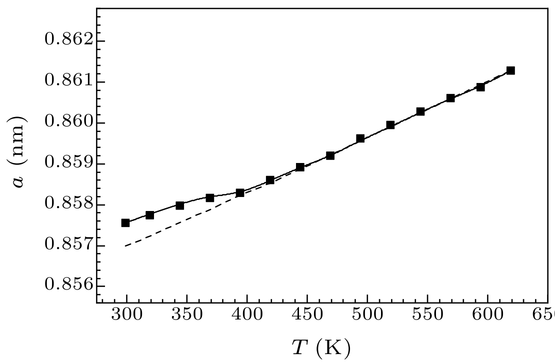

Fig. 4. Temperature dependence of the lattice parameter a of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound. The dashed line represents the values extrapolated from the paramagnetic range.

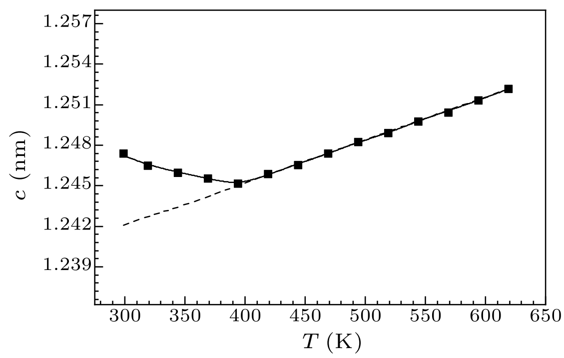

Fig. 5. Temperature dependence of the lattice parameter c of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound. The dashed line denotes the values extrapolated from the paramagnetic range.

The temperature dependences of lattice parameters a and c of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample are shown in Figs. 4 and 5. It is obvious that the negative volume thermal expansion of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample in the temperature range from 299 to 394 K is anisotropic, and the NTE occurs mainly along the c axis.

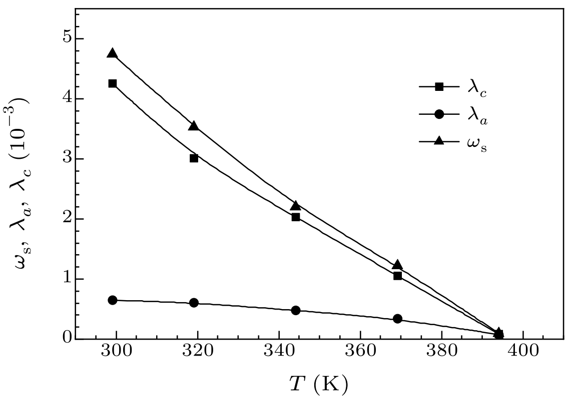

Fig. 6. Temperature dependences of the spontaneous volume magnetostrictive deformation ω_s and the spontaneous linear magnetostrictive deformations λ_a and λ_c of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound.

The temperature dependences of the extrapolated values v_p, a_p, and c_p of the $Nd_2Fe_{16.5}Cr_{0.5}$ sample are given in Figs. 3–5. As in Refs. [6–11,13–15] one can derive the temperature dependence of the spontaneous volume magnetostrictive deformation ω_s from the relationship $\omega_s = (v_m - v_p)/v_p$, and the temperature dependences of the spontaneous linear magnetostrictive deformations λ_a in the basal-plane and λ_c along the c axis from the relationships: $\lambda_a = (a_m - a_p)/a_p$, and $\lambda_c = (c_m - c_p)/c_p$, respectively. Here m and p represent the magnetic state and the paramagnetic state, respectively. The temperature dependences of ω_s, λ_a and λ_c are shown in Fig. 6. It is indicated that the value of ω_s decreases monotonically with temperature increasing from about 4.74×10^{-3}/K at 299 K to 0.10×10^{-3}/K at 394 K, and the value of λ_c decreases monotonically from about 4.26×10^{-3}/K at 299 K to 0.08×10^{-3}/K at 394 K. This is similar to that of the $Dy_2Fe_{16}Cr$[15] and $Gd_2Fe_{16}Cr$ compounds.[10] It is obvious that the value of λ_a is much smaller than that of λ_c, and decreases slightly with temperature increasing below 370 K. This means that the spontaneous volume magnetostrictive deformation ω_s is anisotropic, and mainly comes from the spontaneous linear deformation λ_c along the c axis.

The $Nd_2Fe_{16.5}Cr_{0.5}$ compound has a rhombohedral Th_2Zn_{17}-type structure. The Curie temperature of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound is higher than that of the Nd_2Fe_{17} compound. There is a small negative thermal expansion coefficient of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound in a broad temperature range from 299 K to 394 K, and there exists anisotropic and spontaneous magnetostriction in the magnetic state of the $Nd_2Fe_{16.5}Cr_{0.5}$ compound.

References

[1] Mary T A, Evans J S O, Vogt T and Sleight A W 1996 *Science* **272** 90
[2] Gębara P, Cesnek M and Bednarcik J 2019 *Curr. Appl. Phys.* **19** 188
[3] Song Y Z, Chen J, Liu X Z, Wang C W, Zhang J, Liu H, Zhu H, Hu L, Lin K, Zhang S T and Xing X R 2018 *J. Am. Chem. Soc.* **140** 602
[4] Wang H P, Zhao J F, Liu W and Wei B 2018 *J. Appl. Phys.* **124** 215107
[5] Lagarec K and Rancourt D G 2000 *Phys. Rev. B* **62** 978
[6] Hao Y M, Zhao M and Zhou Y 2005 *J. Appl. Phys.* **98** 076101
[7] Hao Y M, Zhang X M, Wang B W, Yuan Y Z and Wang F 2010 *J. Appl. Phys.* **108** 023915
[8] Hao Y M, Liang F F, Zhang X M, Wu Y Z, Qin H W and Hu J F 2011 *IEEE Trans. Magn.* **47** 3614
[9] Hao Y M, Zhou Y and Zhao M 2005 *J. Appl. Phys.* **97** 116102
[10] Hao Y M, Zhao M, Zhou Y and Hu J 2010 *Chin. Phys. B* **19** 067502 DOI: 10.1088/1674-1056/19/6/067502
[11] Hao Y M, Zhao M, Zhou Y and Hu J 2006 *Eur. Phys. J. Appl. Phys.* **33** 103
[12] Gao C, Hao Y, Liang F, Zhen K and Hu H 2012 *J. Chin. Rare-Earth Soc.* **30** 699 (in Chinese)
[13] Hao S Q, Chen N X and Shen J 2002 *J. Magn. Magn. Mater.* **246** 115
[14] Hao Y M, Zhao M, Zhou Y and Hu J F 2005 *Scr. Mater.* **53** 357
[15] Hao L Y, Yang T, Wang X T and Tan M 2019 *Chin. Phys. Lett.* **36** 066501