Negative Thermal Expansion of the $Dy_2Fe_{16}Cr$ Compound *

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(Received 12 April 2019)

Structural, thermal expansion, and magnetic properties of the $Dy_2Fe_{16}Cr$ compound are investigated by means of x-ray diffraction and magnetization measurements. The $Dy_2Fe_{16}Cr$ compound has a hexagonal Th_2Ni_{17}-type structure. There exists a negative thermal expansion resulting from a strong spontaneous magnetostriction in the magnetic state of the $Dy_2Fe_{16}Cr$ compound. The average thermal expansion coefficient is $-0.794 \times 10^{-5}/K$ in the temperature range 292–407 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/36/6/066501

Materials with negative thermal expansion (NTE) and their composites with other materials have been widely used in the fields of precision instruments, aerospace, and many other fields, thus a large number of theoretical and experimental studies have been carried out.[1–4] In recent decades,[5–8] it was found that there exists an NTE of rare-earth transition metal compounds of R_2T_{17}, where R is rare-earth elements, and T is transition metal elements. For example, in the $Tb_2Fe_{16}Cr$ compound with hexagonal Th_2Ni_{17}-type structure,[9] the NTE occurs in the temperature range from 293 K to 550 K. Especially for the $Gd_2Fe_{16}Cr$ compound with rhombohedral Th_2Zn_{17}-type structure,[10] the NTE was found in a broad temperature range from 292 to about 570 K. This makes the application of these compounds possible. Thus it is necessary to further study the thermal expansion property of the R_2T_{17} compound. In a previous study,[11] it was found that the substitution of one Cr atom for one Fe atom can increase the Curie temperature of the Dy_2Fe_{17} compound. To investigate the NTE in a broad temperature range, in this work, the thermal expansion behavior and its spontaneous magnetostrictions of the $Dy_2Fe_{16}Cr$ compound from 292 K to 632 K are investigated by means of x-ray dilatometry and magnetization measurements.

The raw materials of Dy, Fe, and Cr used in the experiment were of at least 99.98% purity. The compound of $Dy_2Fe_{16}Cr$ 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 glass tube, then annealed at 1373 K for five days. After that, it was quenched in water, then the ingot was ground into powder. To decrease the stress, the powder was sealed in a silicon vacuum tube, annealed at 573 K 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. The Curie temperature T_c was derived from the temperature dependence of the magnetization curve measured by a vibrating sample magnetometer in a field of 40 kA/m. The thermal expansion was measured by x-ray dilatometry. For the determination of the lattice parameters a and c of the $Dy_2Fe_{16}Cr$ compound in the temperature range from 292 to 632 K, the powder sample was placed into an evacuated high-temperature chamber and step scanning (in steps of 0.001°) x-ray diffraction patterns of the (112) and (302) 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, $C_v(T/T_D) = 9R(\frac{T}{T_D})^3 \int_0^{T_D/T} \frac{\xi^4 e^\xi}{(e^\xi-1)^2} d\xi$, and the Grüneisen relation, $\alpha(T) = \frac{\gamma C_v}{K_0 V}$, with C_v being the specific heat, T the temperature, T_D the Debye temperature, R the molar gas constant, α the thermal expansion coefficient, γ the Grüneisen parameter, K the modulus of elasticity, and V the unit-cell volume. The Debye temperature 400 K of the R_2Fe_{17} compound was used to extrapolate the temperature dependence of the lattice parameters of the sample; see Refs. [8-10].

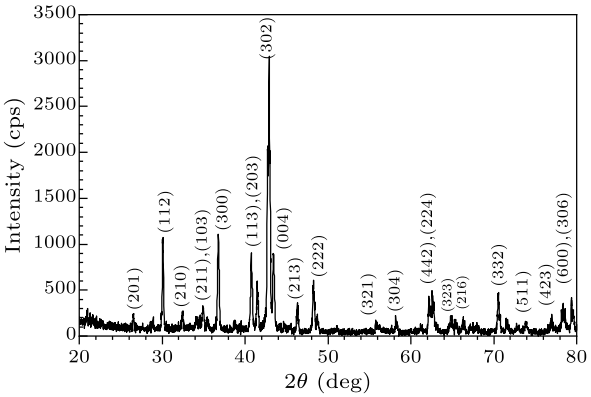

Fig. 1. The x-ray diffraction pattern of the $Dy_2Fe_{16}Cr$ sample at room temperature (about 300 K).

The x-ray diffraction pattern (at 0.02° intervals) of

*Supported by the National Natural Science Foundation of China under Grant Nos 50871074 and 61474082.
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the $Dy_2Fe_{16}Cr$ sample at room temperature is shown in Fig. 1. The indices of the crystallographic plane (hkl) of reflections are marked on the peaks correspondingly. It is obvious that the $Dy_2Fe_{16}Cr$ compound is in a single phase with a hexagonal Th_2Ni_{17}-type structure (space group, $P6_3/mmmc$). The lattice parameters a and c, and the unit-cell volume v are 0.84500 nm, 0.83295 nm, and 0.51506 nm^3, respectively.

Figure 2 shows the temperature dependence of magnetization of the $Dy_2Fe_{16}Cr$ sample. It is indicated that only one magnetic phase exists in the sample. From Fig. 2, one can estimate the Curie temperature of the $Dy_2Fe_{16}Cr$ compound to be about 438 K. This value is about 70 K higher than that of the mother compound Dy_2Fe_{17}.[11] As with the $Y_2Fe_{15}Cr_2$ compound,[12] this may be attributed to the Cr atom preferring to occupy the $4f$ sites of the Th_2Ni_{17}-type structure.

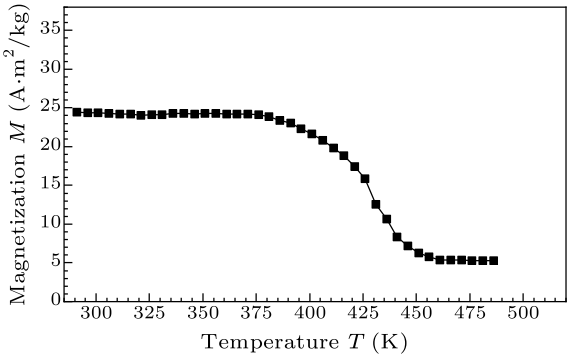

Fig. 2. Temperature dependence of the magnetization of the $Dy_2Fe_{16}Cr$ sample in a field of 40 kA/m.

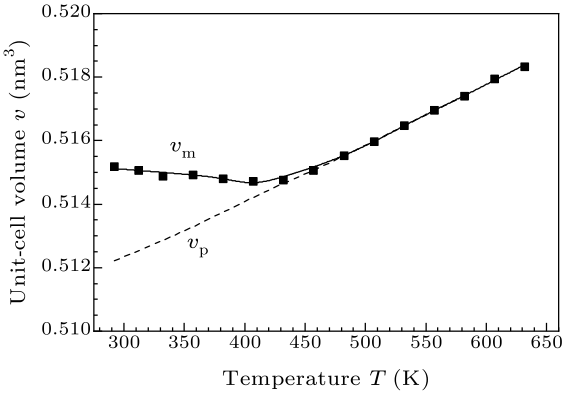

Fig. 3. Temperature dependence of the unit-cell volume v of the $Dy_2Fe_{16}Cr$ compound. The dashed line represents the values extrapolated from the paramagnetic range according to the Debye theory and the Grüneisen relation.

The x-ray diffraction of $Dy_2Fe_{16}Cr$ indicates that the sample is still in a single phase with hexagonal Th_2Ni_{17}-type structure from 292 K to 632 K. Figure 3 gives the temperature dependence of the unit-cell volume v of the $Dy_2Fe_{16}Cr$ sample. It is obvious that there is a negative volume thermal expansion of the $Dy_2Fe_{16}Cr$ sample in the temperature range of 292–407 K.

If the variation of the rate of v is considered in the temperature range from 292 K to 632 K, we can obtain the average thermal expansion coefficients, $\bar{\alpha} = \frac{\Delta v}{\Delta T \bar{v}} = -0.794 \times 10^{-5}/\mathrm{K}$ in the temperature range of 292–407 K, and $3.11 \times 10^{-5}/\mathrm{K}$ in the temperature range of 407–632 K, respectively. Just as in the $Tb_2Fe_{16}Cr$ and $Gd_2Fe_{16}Cr$ compounds,[9,10] this NTE in the temperature range of 292–407 K is ascribed to the existence of a strong magneto-volume effect in the $Dy_2Fe_{16}Cr$ compound.

Figure 4 shows the temperature dependences of lattice parameters a and c. It means that the negative volume thermal expansion of the sample in the temperature range from 292 to 407 K is anisotropic, and that the NTE occurs mainly along the c-axis.

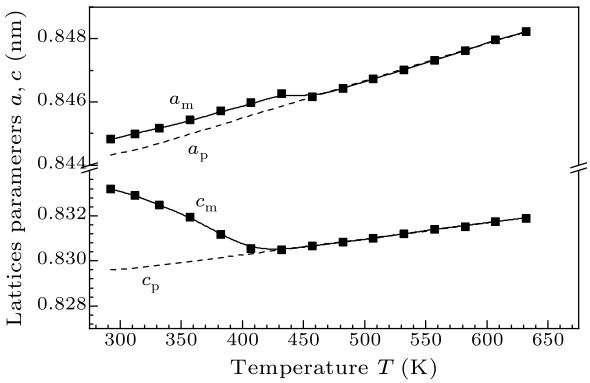

Fig. 4. Temperature dependences of the lattice parameters a and c of the $Dy_2Fe_{16}Cr$ compound. The dashed line represents the values extrapolated from the paramagnetic range according to the Debye theory and the Grüneisen relation.

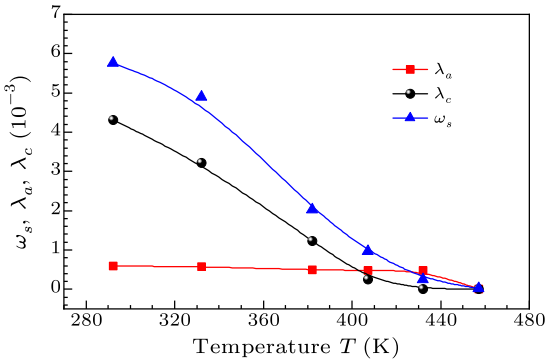

Fig. 5. Temperature dependences of the spontaneous volume magnetostrictive deformation ω_S and the spontaneous linear magnetostrictive deformations λ_a and λ_c of the $Dy_2Fe_{16}Cr$ compound.

The temperature dependences of the extrapolated values v_p, a_p, and c_p are given in Figs. 3 and 4. As in Refs. [8-10,13], 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, where subscripts m and p represent the magnetic state and the paramagnetic state, respectively. Figure 5 shows the temperature dependences of λ_a, λ_c, and ω_s. It is indicated that the value of ω_s decreases

from about 5.76×10^{-3}/K at 292 K to 0.97×10^{-3}/K at 407 K, and the value of λ_c decreases from about 4.31×10^{-3}/K at 292 K to 0.25×10^{-3}/K at 407 K. This is similar to that of the $Gd_2Fe_{16}Cr$ compound.[10] Figure 5 also shows that the value of λ_a is much smaller than that of λ_c, and decreases slightly with increasing the temperature below 407 K. This implies that the spontaneous volume magnetostrictive deformation ω_s comes mainly from the spontaneous linear magnetostrictive deformation λ_c along the c-axis.

In summary, we can conclude that there exists an anisotropic and strong spontaneous magnetostrictive effect in the $Dy_2Fe_{16}Cr$ compound. NTE behavior appears in the temperature range from 292 to 407 K.

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