Anomalous thermal expansion and spontaneous magnetostriction of $Gd_2Fe_{16}Cr$ compound*

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The structural and the magnetic properties of $Gd_2Fe_{16}Cr$ compound are investigated by x-ray diffraction and magnetization measurements. The $Gd_2Fe_{16}Cr$ compound has a rhombohedral Th_2Zn_{17}-type structure. There exist an anisotropic strong spontaneous magnetostriction and a negative thermal expansion in the magnetic state of $Gd_2Fe_{16}Cr$ compound. The average thermal expansion coefficient $\bar{\alpha} = -7.03 \times 10^{-6}$/K in a temperature range of 294–454 K and $\bar{\alpha} = -1.31 \times 10^{-5}$/K in 454–572 K are obtained. The spontaneous magnetostrictive deformation and the Curie temperature are discussed.

Keywords: x-ray diffraction, intermetallic compound, negative thermal expansion, magnetostriction

PACC: 7550B, 7530C

1. Introduction

Materials with zero thermal expansion (ZTE) coefficients are very useful for improving the geometrical stabilities of aeronautic and astronautic structures, electric and optical devices as well as structural materials under high thermo-mechanical load.[1] Unfortunately, there exist a few of these materials actually. Usually materials with negative thermal expansion (NTE) coefficients are used as constituents of composite materials designed to achieve a desired overall thermal expansion coefficient. However, these materials with negative thermal expansion coefficients are known in only several oxide systems and a few Invar alloys.[1−3] When the negative thermal expansion occurs, the contraction is usually small and limited to a narrow temperature range beyond room temperature. The finding of the new materials with negative thermal expansion coefficients and the further understanding of the mechanism may, therefore, play an important role in both theory and application.

In recent years, it has been found that there exists a negative thermal expansion of R_2T_{17} (R is rare-earth elements, T is transition metal elements) compounds with the hexagonal Th_2Ni_{17}-type structure near its Curie temperature,[4−6] especially for $Tb_2Fe_{16}Cr$ compound with the hexagonal Th_2Ni_{17}-type structure.[7] The negative thermal expansion occurs in a broad temperature range from 293 K to 550 K. This probably makes it possess some practical uses. Thus, researchers are interested in the study of rare-earth (R)-iron intermetallic compounds with Th_2Ni_{17} or Th_2Zn_{17} structure.

In the previous investigations,[8,9] it was found that the substitution of one Cr atom for one Fe atom can increase greatly the Curie temperature of R_2Fe_{17} compound. To investigate the negative thermal expansion in a broad temperature range, in this work, the thermal expansion behaviour of the unit-cell volume of $Gd_2Fe_{16}Cr$ compound with rhombohedral Th_2Zn_{17}-type structure from 294 K to 692 K is investigated by x-ray dilatometry.

2. Experiment

The $Gd_2Fe_{16}Cr$ compound was prepared by arc melting in an argon atmosphere of high purity. The raw materials of Gd, Fe, and Cr were at least 99.99% purity. The ingot was re-melted four times to ensure its homogeneity. The arc-melted ingot was sealed in a silica vacuum tube, annealed at 1050 ℃ for 5 d, and then quenched in water. The ingot annealed was ground into powder. To decrease the stress in the sam-

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ple, the powder was sealed in a silica vacuum tube, annealed at 300 °C for 5 h and then slowly cooled down to room temperature. The powder x-ray diffraction with Cu K_α radiation was used to examine the phase structure of the sample. For the determination of the lattice parameters a and c of the $Gd_2Fe_{16}Cr$ compound in a temperature range from 294 K to 692 K, step scanning (in steps of 0.1°) x-ray diffraction pattern of the (113) and (303) reflections were recorded by an 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 ω_S, λ_a, λ_c were determined by the differences between the experimental values v_m, a_m, c_m of the lattice parameters at a given temperature and the corresponding values v_p, a_p, c_p extrapolated from the paramagnetic range according to Debye theory and Grüneisen relation. The values of the Debye temperature T_D, which are necessary for the extrapolation, were estimated from acoustic measurements to be 450 K for Y_2Fe_{17} and 400 K for the other R_2Fe_{17} compounds.[10] The same value 400 K was used to extrapolate the temperature dependences of the lattice parameters of the sample.

The value of Curie temperature T_C of the $Gd_2Fe_{16}Cr$ compound was derived from the temperature dependence of magnetization curve by a vibrating sample magnetometer (VSM) in a low field 40 kA/m.

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern of $Gd_2Fe_{16}Cr$ sample at room temperature (about 300 K). It is indicated that the $Gd_2Fe_{16}Cr$ compound is in a single phase with a rhombohedral Th_2Zn_{17}-type structure (space group, $R\bar{3}m$). The indices of crystallographic plane (h k l) of reflections are marked on the peaks correspondingly. The unit-cell volume v and the lattice parameters a and c are 0.77367 nm^3, 0.85030 nm, and 1.23569 nm, respectively. They are in agreement with the values calculated from the x-ray diffraction patterns of (113) and (303) reflections, which are 0.77369 nm^3, 0.85036 nm, and 1.23559 nm, respectively.

The temperature dependence of magnetization of the $Gd_2Fe_{16}Cr$ sample in a low field 40 kA/m is given in Fig. 2. It is obvious that only one magnetic phase exists in the sample. From Fig. 2 one can estimate the Curie temperature of the $Gd_2Fe_{16}Cr$ compound to be about 575 K. This value is about 70 K higher than the Curie temperature of the mother compound Gd_2Fe_{17} with the rhombohedral Th_2Zn_{17}-type structure.[11] In the neutron-diffraction study of $Y_2Fe_{15}Cr_2$ compound and the theoretical study of Nd_2Fe_{17-x} Cr_x compounds,[8,12] it was found that Cr atom preferred to occupy the 4f/6c sites. It is known that there is an anti-ferromagnetic interaction between Fe atoms at 4f/6c sites in R_2Fe_{17} compound. The substitution of the weaker magnetic atom Cr for the stronger magnetic atom Fe on 4f/6c sites may reduce the strength of the anti-ferromagnetic interaction at 4f/6c sites and increase the total strength of the ferromagnetic interaction of the unit-cell. The ferromagnetic exchange interaction directly affects the magnetic ordering temperature T_C. This may provide an explanation for the increase of the Curie temperature of $Gd_2Fe_{16}Cr$ compound, just as in $Y_2Fe_{17-x}Cr_x$ compound.[8]

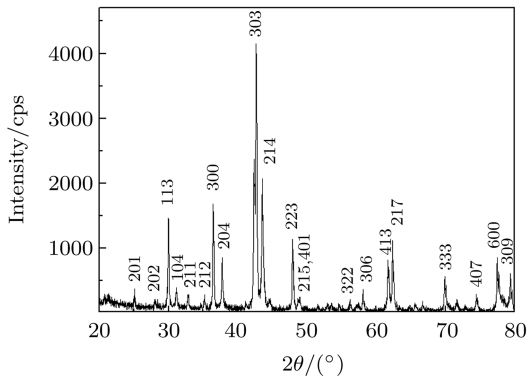


Fig. 1. The x-ray diffraction pattern of $Gd_2Fe_{16}Cr$ sample at room temperature (∼300 K).

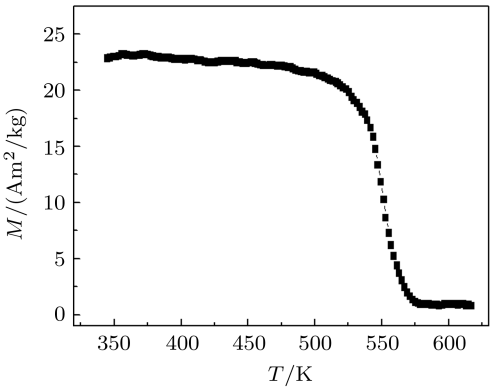


Fig. 2. Temperature dependence of the magnetization of $Gd_2Fe_{16}Cr$ sample in a field of 40 kA/m.

The x-ray diffractions of the $Gd_2Fe_{16}Cr$ sample from 294 K to 692 K indicate that the sample is still in a single phase with the rhombohedral Th_2Zn_{17}-type structure from 294 K to 692 K.

The diffraction angles (2θ) of the highest intensity of x-ray diffraction peaks (113) and (303) are determined by refining the simulation of the peaks of (113) and (303) with using a Gauss-type function. The values of distance d between the crystal faces (113) and between the crystal faces (303) are determined from the formulation, $2d\sin\theta = \lambda$, where λ is the wavelength of Cu K_α radiation. The lattice constants a and c are determined from the formula, $1/d^2 = 4(h^2+hk+k^2)/3a^2+l^2/c^2$. Here, h, k and l are the indices of the crystallographic plane (h k l). The unit-cell volume v is calculated from $v = \sqrt{3}a^2c/2$. Figure 3 shows the temperature dependence of unit-cell volume v of the $Gd_2Fe_{16}Cr$ sample. It shows that there is a temperature range with a negative coefficient of thermal expansion in $Gd_2Fe_{16}Cr$ sample. This temperature range is broader than that in other compounds.[6,13–15] The values of negative coefficients ($\bar{\alpha}$) and its temperature ranges (ΔT_1) of other compounds are shown in Table 1. Otherwise, if the variation of the rate of v is considered from 294 K to 692 K, we have average thermal expansion coefficients, i.e.

$$\bar{\alpha} = \frac{\Delta v}{v\Delta T} = -7.03 \times 10^{-6}/\mathrm{K}$$

in a temperature range of 294 K–454 K, $\bar{\alpha} = -1.31 \times 10^{-5}$/K in 454 K–572 K, and $\bar{\alpha} = 8.94 \times 10^{-5}$/K in 572 K–692 K, respectively. It is obvious that the absolute value of the thermal expansion coefficient in the temperature range 454 K–572 K is larger than that in 294 K–454 K. Just as in $Tb_2Fe_{16}Cr$ compound with the hexagonal Th_2Ni_{17}-type structure,[7] this existence of negative thermal expansion behaviour may indicate that there is strong magneto-volume effect in $Gd_2Fe_{16}Cr$ compound with the rhombohedral Th_2Zn_{17}-type structure.

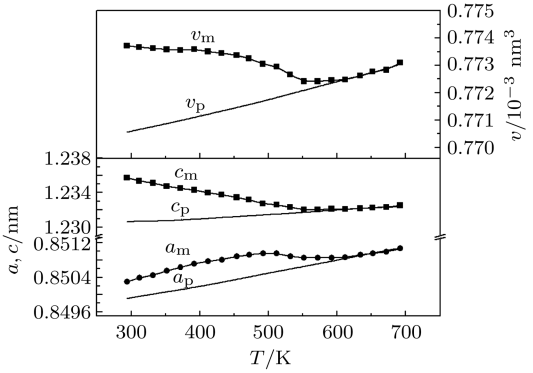


Fig. 3. Temperature dependences of the unit cell volume v and the lattice parameters a and c of $Gd_2Fe_{16}Cr$ compound. The solid line represents the contribution of phonons to the thermal expansion.

In the magnetic state of $Gd_2Fe_{16}Cr$ compound, just as in $Y_2Fe_{14}Al_3$ compound,[6] there are two reasons for the changing of unit-cell volume with temperature increasing. One is the magnetic ordering. Both ferromagnetic interaction and spontaneous magnetic moment decrease with temperature increasing, which leads to the contracting of unit-cell volume. The other reason comes from the normal thermal expansion effect (in other words, the phonon contribution to the thermal expansion), which results in expansion of the unit-cell volume with temperature increasing. This may provide an explanation for the thermal expansion coefficients at low temperatures. The influence caused by magnetic ordering on the thermal expansion is superior to the phonon contribution below 572 K, and hence the negative thermal expansion behaviour appears. Otherwise, the negative thermal expansion behaviour below 454 K mainly comes from the decreasing of the ferromagnetic magnetic interactions, and the negative thermal expansion behaviour from 454 K to 572 K results not only from the decreasing of the ferromagnetic magnetic interactions but also from the sharp decreasing of the spontaneous magnetic moment. This can be seen in Fig .2. It shows that the magnetic moment rapidly drops from about 470 K. In a high temperature range (above 572 K), there is only normal thermal expansion effect, and hence the thermal expansion coefficient is positive.

Figure 3 also shows the temperature dependences of lattice parameters a and c. It means that the thermal expansion of $Gd_2Fe_{16}Cr$ compound at low temperatures (i.e. in a magnetic state) is anisotropic.

The temperature dependences of the extrapolated values v_p, a_p, and c_p are given in Fig. 3. We 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_c along the c axis and λ_a in the basal-plane from the relationships: $\lambda_c = (c_m c_p)/c_p$ and $\lambda_a = (a_m a_p)/a_p$, respectively. Here m and p represent the magnetic state and the paramagnetic state, respectively. The temperature dependences of ω_S, λ_c and λ_a are shown in Fig. 4. It is obvious that the value of ω_S decreases from about 4.18×10^{-3} to near zero with temperature increasing from 294 K to 572 K and the decreasing rate of the ω_S above 450 K is faster than that below 450 K. It is suggested that the variation of ω_S above 450 K may be due to not only the decreasing of the ferromagnetic magnetic interaction, but also

the loss of the average magnetic moment. Otherwise, the variation of ω_S below 450 K may be mainly because of the decreasing of the ferromagnetic magnetic interaction. The temperature dependences of λ_c and λ_a are also shown in Fig. 4. It is noticed that spontaneous linear deformation λ_c is much larger than λ_a at the same temperature except near to the Curie temperature. The difference between λ_c and λ_a is the same as that in other R_2(Fe, Al, Mn)$_{17}$ compounds with Th_2Ni_{17}-type structure.[6,13–15] The changes of λ_c, λ_a and their difference (λ_c–λ_a) in the temperature ranges (ΔT_2) in other compounds are shown in Table 1. This implies that the strength of magnetoelastic effect along the c axis is much stronger than that in the basal-plane. Below 450 K, λ_a increases slightly with temperature increasing. It implies that the total ferromagnetic interaction in the basal-plane is enhanced slightly with temperature increasing. Just as in $Dy_2AlFe_{10}Mn_6$ compound,[16] this may be due to the fact that the decreasing of the anti-ferromagnetic interaction between Fe and Cr atoms is faster than the decreasing of the ferromagnetic interaction between Fe and Fe atoms with temperature increasing.

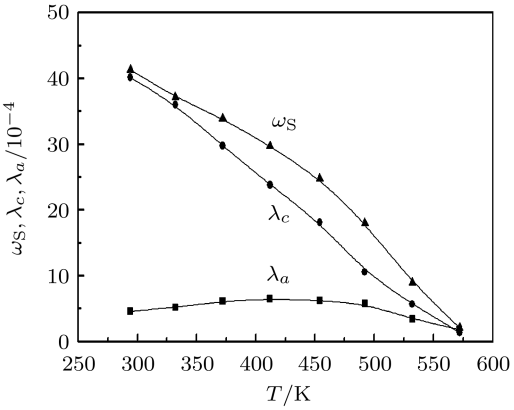


Fig. 4. Temperature dependences of the spontaneous volume magnetostrictive deformation ω_S and the spontaneous linear magnetostrictive deformations λ_c and λ_a of $Gd_2Fe_{16}Cr$ compound.

Table 1. Values of average thermal expansion coefficient $\bar{\alpha}$ in temperature variation range ΔT_1 and values of λ_c, λ_a, and (λ_c–λ_a) in temperature range ΔT_2 for some R_2(Fe, Al, Mn)$_{17}$ compounds.

compounds	$Y_2Fe_{14}Al_3$[6]	$Dy_2AlFe_{13}Mn_3$[13]	$Y_2Fe16Al$[14]	$Er_2AlFe_{15}Mn$[15]	$Gd_2Fe_{16}Cr$	
ΔT_1/K	403∼91	245∼344	332∼438	342∼403	294∼454	454∼572
$\bar{\alpha}/10^4$ K^{-1}	–0.25	–1.1	–0.34	–0.20	–0.07	–0.13
ΔT_2/K	283∼470	105∼350	293∼427	103∼390	294∼572	
$\lambda_c/10^{-3}$	2.5∼0.2	5.1∼0.1	5.8∼0.2	4.8∼0.2	4.0∼0.2	
$\lambda_a/10^{-3}$	1.1∼0.1	0.8∼0.1	2.4∼0.3	1.8∼0.6	0.5∼0.2	
$(\lambda_c - \lambda_a)/10^{-3}$	1.4∼0.1	4.3∼0	3.4∼–0.1	3.0∼–0.4	3.5∼0	

4. Conclusion

There is a negative thermal expansion coefficient for $Gd_2Fe_{16}Cr$ compound with a rhombohedral Th_2Zn_{17}-type structure in a broad temperature range from 294 K to 572 K, and there exists anisotropic strong and spontaneous magnetostriction in the magnetic state of $Gd_2Fe_{16}Cr$ compound. In $Gd_2Fe_{16}Cr$ compound with the rhombohedral Th_2Zn_{17}-type structure, one Cr atom substituting for one Fe atom can increase obviously the Curie temperature.

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