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Thermal expansion anomaly and spontaneous magnetostriction of $Dy_2AlFe_{14}Mn_2$ compound

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Abstract: The structure and magnetic properties of $Dy_2AlFe_{14}Mn_2$ compound were investigated by X-ray diffractometry and magnetization measurements. $Dy_2AlFe_{14}Mn_2$ compound has a hexagonal Th_2Ni_{17}-type structure. Zero thermal expansion and negative thermal expansion were found in $Dy_2AlFe_{14}Mn_2$ compound in the temperature range from 184 to 264 K, and from 264 to 383 K, respectively, by X-ray dilatometry. The spontaneous magnetostrictive deformations from 104 to 400 K were calculated. The results show that the spontaneous volume magnetostrictive deformation increases firstly with increasing temperature, and then decreases with further increasing temperature.

Key words: $Dy_2AlFe_{14}Mn_2$ compound; thermal expansion; spontaneous magnetostriction; negative thermal expansion

1 Introduction

The materials with negative thermal expansion have many important applications. These materials are known only in several oxide systems[1,2] and a few Invar alloys[3]. When the negative thermal expansion occurs, the contraction is usually small and limited to a narrow temperature range that does not include room temperature. Notable exceptions are ZrW_2O_8 and HfW_2O_8 with cubic phase of the type ZrW_2O_8, which show negative thermal expansion over a very broad temperature range (which is from 0.3 to 1 050 K)[3,4]. The discovery of the new materials with a negative coefficient of thermal expansion and further insights into the mechanism may, therefore, play an important role in theory and applications.

The relatively low Curie temperature for the binary rare-earth(RE)-iron intermetallic compounds with Th_2Zn_{17} or Th_2Ni_{17} structure and the fact that none of them exhibits an easy-axis anisotropy at room temperature restrict the possible application of these materials as permanent magnets[5−7]. Numerous investigations have been made to improve their magnetic properties. The discoveries that the introduction of nitrogen or carbon in RE_2Fe_{17} leads to a dramatic increase of the Curie temperature and that nitrogenation of Sm_2Fe_{17} changes the magnetocrystalline anisotropy `from basal to axial make these compounds to be potentially interesting materials for permanent magnets[8,9].

Recent attention has focused on the magnetic substitution of Mn on the magnetic and structural properties of RE_2Fe_{17}[7−17]. It was found that the Curie temperatures of Mn-substituted RE_2Fe_{17} compounds decreased fast. However they show a large positive spontaneous volume magnetostriction in magnetic states, which leads to a large negative volume change near their Curie temperatures. For example, in $Y_2Al_3Fe_{11}Mn_3$ compound[13], the average thermal expansion coefficient is $\bar{\alpha}=\Delta V/(V\Delta T)\approx-7.5\times10^{-5}$/K in the temperature range of 185−200 K. This makes these materials interesting from both a fundamental point of view and applications for negative thermal expansion materials.

In this work, the thermal expansion behavior of the unit-cell volume of $Dy_2AlFe_{14}Mn_2$ compound from 104 to 647 K and its spontaneous magnetostrictions are

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investigated by means of X-ray dilatometry and magnetization measurements.

2 Experimental

The compound of $Dy_2AlFe_{14}Mn_2$ was prepared by arc melting in an argon atmosphere of high purity. The raw materials of Dy, Fe, Mn and Al have at least a purity of 99.95%. The ingot was re-melted at least three times to ensure its homogeneity and sealed in a silicon vacuum tube, then annealed at 950 ℃ for 7 d, and after that quenched in water. The ingot was ground into powder. To decrease the stress, the powder was sealed in a silicon vacuum tube, annealed at 300 ℃ for 5 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 SQUID in a low field of 40 kA/m.

The thermal expansion was measured by X-ray dilatometry on a diffractometer. For the determination of the lattice parameters a and c of the $Dy_2AlFe_{14}Mn_2$ compound at 104 to 647 K, the sample was placed into an evacuated chamber, and the step scanning (at 0.01° interval) X-ray diffraction patterns of the (112) and (222) reflections were recorded by 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 means of 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 value of Debye temperature T_D, which is necessary for the extrapolation, was estimated from acoustical measurements to be 450 K for Y_2Fe_{17} and 400 K for other RE_2Fe_{17} compounds[18]. In this experiment the same value 400 K was used for the extrapolation of the temperature dependences of the lattice parameters of the sample.

3 Results and discussion

The XRD pattern of $Dy_2AlFe_{14}Mn_2$ compound at 300 K is shown in Fig.1. The indices of crystallographic plane(*hkl*) of reflections are shown in Fig.1. It indicates that $Dy_2AlFe_{14}Mn_2$ compound is in a single phase with the Th_2Ni_{17}-type structure.

Fig.2 shows the temperature dependence of the magnetization of $Dy_2AlFe_{14}Mn_2$ compound in a low magnetization field of 40 kA/m, from which the Curie temperature of the sample can be derived at about 350 K.

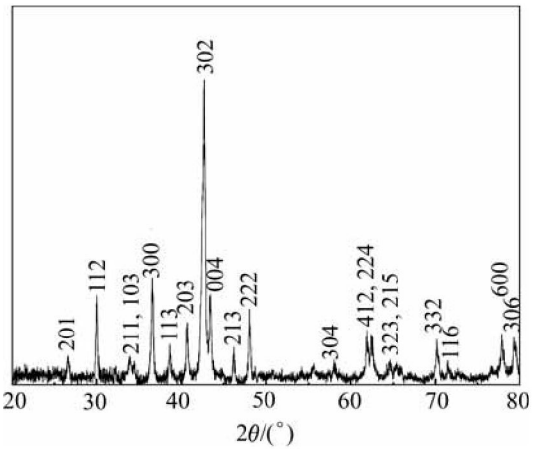

Fig.1 X-ray pattern of $Dy_2AlFe_{14}Mn_2$ compound at 300 K

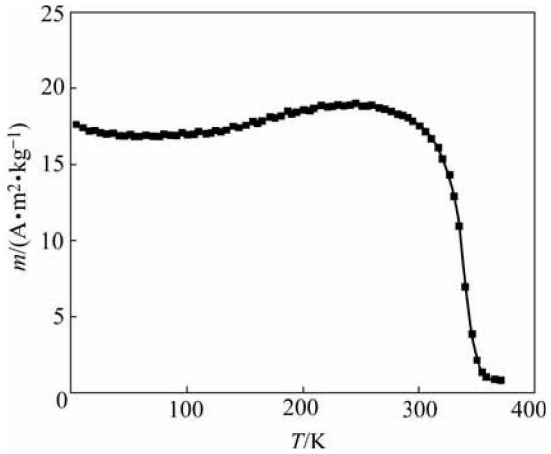

Fig.2 Temperature dependence of magnetization of $Dy_2AlFe_{14}Mn_2$ compound in low magnetization field (40 kA/m)

The temperature dependence of the unit cell volume (v) of $Dy_2AlFe_{14}Mn_2$ compound is shown in Fig.3. If the variation rate of v (v_m) is considered from 104 to 647 K, the average thermal expansion coefficients are $\overline{\alpha}=\Delta V/(V\Delta T)=3.37\times10^{-5}\,K^{-1}$ at 104−184 K, α is near zero at 184−264 K, $\overline{\alpha}=-3.67\times10^{-5}\,K^{-1}$ in 264−383 K, and $\overline{\alpha}=-2.33\times10^{-5}\,K^{-1}$ at 383−647 K, respectively.

It is supposed that the negative thermal expansion behavior from 264 to 383 K results from not only the decrease of the magnetic interaction but also the sharp decrease of the magnetic moment. This can be seen in Fig.2, which shows that the magnetic order rapidly drops from about 265 K. At 184−264 K, the thermal expansion coefficient is near zero. It maybe imply that the magnetic interaction decreases from 184 K with increasing temperature, which leads to a contraction of the unit-cell volume, and the contraction is balanced with the normal thermal expansion. It is obvious that the value of the average thermal expansion coefficient at 104−184 K is larger than that in 383−647K. It is correlated with the increase of the magnetic interaction and magnetic

moment in the temperature range of 104−184 K. It maybe implies that the moment of Mn rotates partly to the moment of Fe with increasing temperature at 104−184 K.

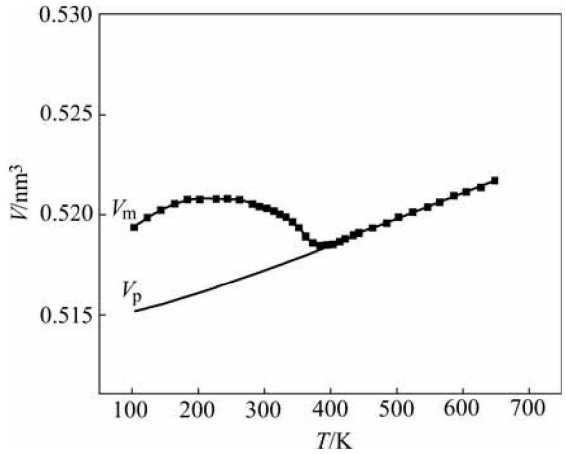

Fig.3 Temperature dependence of unit cell volume of $Dy_2AlFe_{14}Mn_2$ compound

Fig.4 shows the temperature dependences of lattice parameters a and c. This means that the thermal expansion of the sample at 184−383 K is anisotropic.

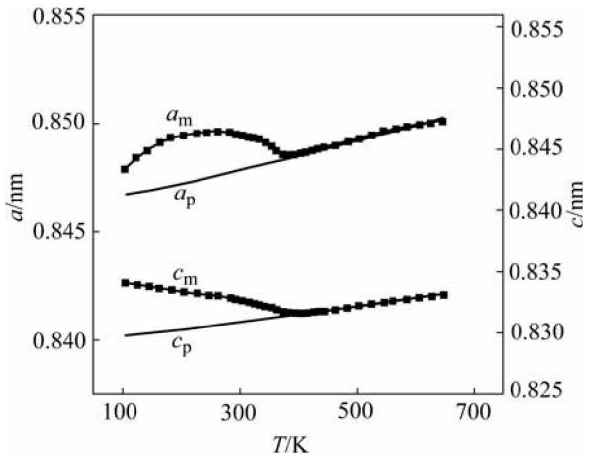

Fig.4 Temperature dependences of lattice parameters a and c of $Dy_2AlFe_{14}Mn_2$ compound

The temperature dependences of the extrapolated values v_p, a_p, and c_p are given in Figs.3 and 4, respectively. From Figs.3 and 4, we can derive the temperature dependence of the spontaneous volume magnetostrictive deformation ω_S by the relation $\omega_S=(v_m-v_p)/v_p$, and the temperature dependences of the spontaneous linear magnetostrictive deformations λ_c along the c axis and λ_a in the basal-plane by the relations $\lambda_c=(c_m-c_p)/c_p$ and $\lambda_a=(a_m-a_p)/a_p$, respectively. Here the signs m and p represent the unit-cell parameters in the magnetic state and paramagnetic state, respectively. The temperature dependence of ω_S is shown in Fig.5. It is obvious that ω_S increases from 8.01×10^{-3} at 104 K to 9.40×10^{-3} at 185 K while then decreases with further increase of temperature. We suppose that the increase of ω_S at 104−185 K is correlated with the increase of the interaction and the magnetic moment of $Dy_2AlFe_{14}Mn_2$ compound. As mentioned above, it maybe imply that the moment of Mn rotates partly to the moment of Fe with increasing temperature. Above 185 K, ω_S decreases with increasing temperature. It may be due to the decrease of magnetic interaction and magnetic moment of $Dy_2AlFe_{14}Mn_2$ compound. ω_S disappears at about 40 K above T_C. This apparently reflects the short-range ordering. The temperature dependences of λ_c and λ_a are also shown in Fig.5. It is noticed that the spontaneous linear magnetostrictive deformation λ_c is larger than λ_a at the same temperature far below T_C, and the λ_c decrease with increasing temperature. The change of λ_a with increasing temperature is complicated. At low temperature ($T<185$ K), λ_a increases from 1.39×10^{-3} at 104 K to 2.64×10^{-3} at 185 K. It maybe imply that the interaction and the magnetic moment in the basal-plane increase. At higher temperature ($T>185$ K), λ_a decreases with increasing temperature. This is due to the decrease of the magnetic interaction and magnetic moment in the basal-plane.

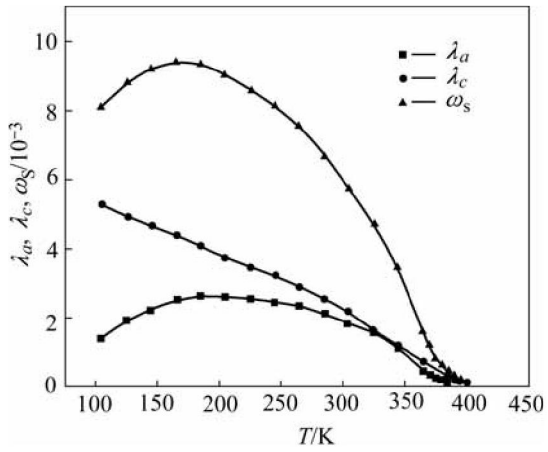

Fig.5 Temperature dependences of spontaneous magnetostrictive deformations ω_S, λ_c, and λ_a of $Dy_2AlFe_{14}Mn_2$ compound

4 Conclusions

For $Dy_2AlFe_{14}Mn_2$ compound, there exists a strong anisotropic spontaneous magnetostriction in its magnetic state, a negative thermal expansion coefficient at 264 to 383 K, and there is a zero thermal expansion from 184 to 264 K.

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