Thermal expansion anomaly and magnetic properties of Nd$_2$AlFe$_{11}$Mn$_5$ compound

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Abstract: Materials with negative thermal expansion have many important applications such as constituents of composite materials designed to reduce their overall thermal expansion. The structural and magnetic properties of Nd$_2$AlFe$_{11}$Mn$_5$ compound were investigated by means of X-ray diffraction and magnetization measurements. The result shows that the Nd$_2$AlFe$_{11}$Mn$_5$ compound crystallizes in a rhomhedral Th$_2$Zn$_{17}$-type structure. The Curie temperature T_c is about 150 K. The negative thermal expansion coefficient of Nd$_2$AlFe$_{11}$Mn$_5$ compound is found by X-ray diffraction in temperature range of 122−203 K. There exists an anisotropic and strong positive spontaneous magnetostriction in Nd$_2$AlFe$_{11}$Mn$_5$ compound. The magnetostriction deformations were discussed.

Key words: Nd$_2$AlFe$_{11}$Mn$_5$ compound; spontaneous magnetostriction; negative thermal expansion

1 Introduction

Materials with negative thermal expansion have many important applications as constituents of composite materials designed to reduce their overall thermal expansion. In 1991, ANDREEV and his co-workers investigated the properties of rare earth(RE)-iron intermetallic compounds based on the type RE$_2$Fe$_{17}$ on the thermal expansion and spontaneous magnetostriction. The result showed that RE$_2$Fe$_{17}$ compounds undergo strong spontaneous magnetostriction(SM) deformations below their Curie temperatures (T_c), which leads to a large negative volume change anomaly near their Curie temperatures[1−4]. Recent attention has focused on the magnetic substitution of Mn and Cr on the magnetic and structural properties of RE$_2$Fe$_{17}$[5−10]. It has been reported that both the T_c and saturation magnetization(M_s) decrease rapidly with increasing x in Pr$_2$AlFe$_{16-x}$Mn$_x$ and Y$_2$Al$_3$Fe$_{14-x}$Mn$_x$ compounds[3, 11]. However, they show a large negative volume change anomaly near T_c. For example, in Y$_2$Al$_3$Fe$_{11}$Mn$_3$ compound[11], the average thermal expansion coefficient is $\bar{\alpha} = \Delta v/(v\Delta T) \approx -7.5 \times 10^{-5}$/K in the temperature range 185−200 K.

In this paper, the thermal expansion behavior of the unit-cell volume of Nd$_2$AlFe$_{11}$Mn$_5$ compound and its magnetic properties are investigated by means of X-ray dilatometry and magnetization measurements. Perhaps the studies on the negative thermal expansion and further insights into the mechanism play an important role in theory and applications.

It has been known that the arc-melted Mn-rich RE$_2$(Fe, Mn)$_{17}$ compound is unstable in the air, and is easy to oxidize. For instance, arc-melted Dy$_2$Fe$_{11}$Mn$_6$ ingot of 12 g is oxidized entirely and becomes gray powder in the air for one day and night[12]. In this work, we substitute one Al atom for one Fe atom in Nd$_2$(Fe,Mn)$_{17}$ compound so that it becomes much steadier than before.

2 Experimental

The Nd$_2$AlFe$_{11}$Mn$_5$ compound was prepared by arc melting starting materials of at least 99.95% purity in argon atmosphere. The ingot was remelted three times to ensure their homogeneity. Afterwards the arc-melted ingot was sealed in an evacuated silica tube. After vacuum annealing for seven days at 950 ℃, the sample was subsequently quenched in cold water. X-ray diffraction(XRD) with Cu K$_\alpha$ radiation was used to check whether the sample was single phase and to

determine the lattice parameters. The experimental error in the determination of a and c was 10^{-4} nm. It has been reported that the normal thermal expansion curves extrapolated from the paramagnetic to the ferromagnetic range can be obtained using the Debye and Grüneisen relation[1, 8]. The value of the Debye temperature T_D, which is necessary for the extrapolation, was estimated from acoustic measurements to be 450 K for Y_2Fe_{17} and 400 K for other RE_2Fe_{17} compounds[13]. We used the same value 400 K for the extrapolation of the temperature dependences of the lattice parameters of the sample.

3 Results and discussion

From the powder X-ray diffraction patterns shown in Fig.1, it can be seen that the annealed sample of $Nd_2AlFe_{11}Mn_5$ compound crystallizes in a rhombohedral structure with Th_2Zn_{17}-type (space group, $R\overline{3}m$), which is as same as $Nd_2Co_9Mn_8$ compound[14]. The indices of crystallographic plane (hkl) of reflections are marked on it. The unit-cell parameters a, c, v of the $Nd_2AlFe_{11}Mn_5$ derived from the whole X-ray pattern are 0.869 2 nm, 1.254 4 nm, and 0.820 9 nm^3, respectively.
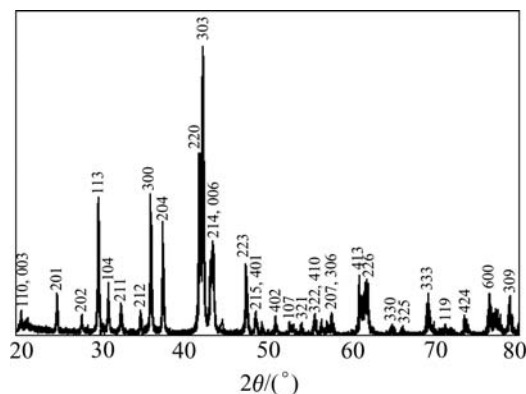

Fig.1 XRD pattern of $Nd_2AlFe_{11}Mn_5$ compound at room temperature

Fig.2 gives the temperature(T) dependence of the magnetization (M) of the $Nd_2AlFe_{11}Mn_5$ compound from 79 to 205 K in a low field of 40 kA/m. It shows that M decreases slowly at the beginning with temperature rising and then drops sharply during the temperature range 130－165 K, and eventually disappears gradually. We confirm that the rapid change in 130－165 K results from the disappearance of magnetic ordering, and it can be also seen in Fig.4. The Curie temperature T_c is about 150 K which is derived by extrapolating square of spontaneous magnetization (M^2) to zero in the plot of M^2 versus T. It is obvious that the T_c value is much lower than that of the

Nd_2AlFe_{16} compound ($T_c \approx 470$ K)[15]. As a rule, we confirm that T_c is determined by the intensity of the exchange interaction and by 3d-sublattice magnetization[2]. Therefore manganese substitution for Fe is likely to reduce the 3d-sublattice magnetization and cause the low T_c value. Otherwise it is possible that the Mn atom substitution for Fe atom reduces the T-T interaction. This may be due to the antiferromagnetic coupling between Mn and Fe in 3d sublattice.
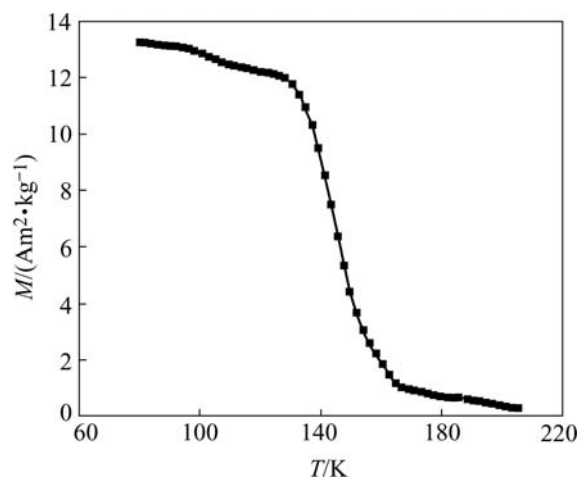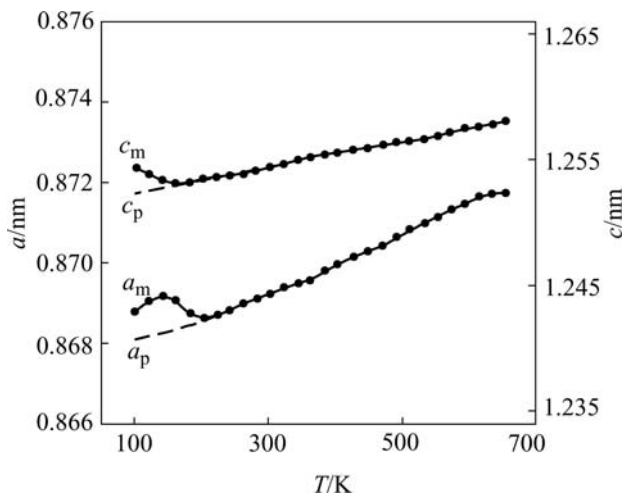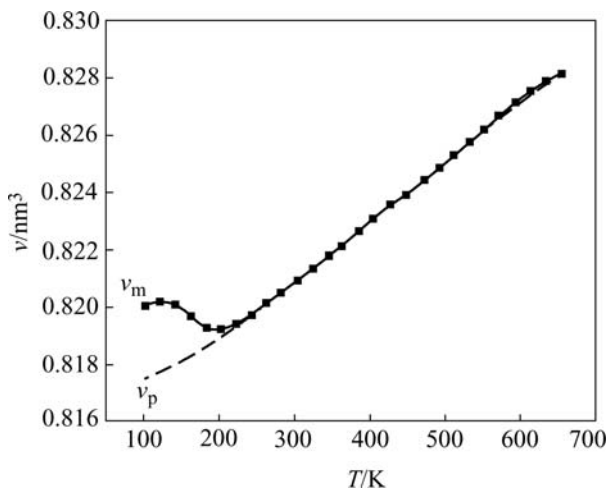

Fig.2 Temperature dependence of magnetization of $Nd_2AlFe_{11}Mn_5$ compound at low field of 40 kA/m

Fig.3 shows the temperature dependence of the lattice parameters a and c of $Nd_2AlFe_{11}Mn_5$ compound which are derived from X-ray diffraction patterns of the (220) and (303) reflections of the rhombohedral lattice with step-scanning (at 0.01° intervals). Along the c axis, the value decreases monotonously with increasing temperature from 103 to 162 K, and then increases linearly above T_c. In the basal plane the variety of parameter a is more complicated. Unlike the transformation of c, it increases at first, and then decreases in the temperature range of 142－203 K. This indicates that the negative thermal expansion is anisotropic. In the magnetic state of $Nd_2AlFe_{11}Mn_5$ compound, there are two reasons working on unit-cell size. One is magnetic ordering which decreases with temperature increasing and brings on the contraction of the 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 the expansion of the unit-cell with temperature increasing. Being at high temperature, there is only normal thermal expansion effect. We suppose that the parameters a and c changed variously is due to the anisotropy of magnetic ordering disappear. Compared with being along c axis, the magnetic ordering in basal plane disappears at higher temperature.
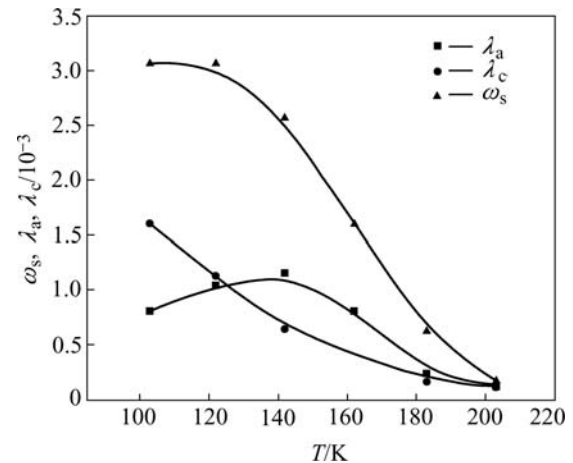
Fig.3 Temperature dependences of lattice parameters a and c of $Nd_2AlFe_{11}Mn_5$ compound(dash lines represent phonon contribution to thermal expansion)

There is a negative thermal expansion behavior in temperature range of $122-203$ K as shown in Fig.4 and the average thermal expansion coefficient is $\bar{\alpha} = \Delta v/(v\Delta T) = -1.7 \times 10^{-5}$/K. Furthermore, the negative thermal expansion of the sample is anisotropic (see Fig.3). Previous studies indicated that in the case of Mn substitution, the Mn atoms preferentially occupy 6c/4f sites of the crystallographic structure. The unusual behavior of the unit-cell volume can be understood by considering the magnetovolume effect in compound even though the influence of the 6c/4f site preferential occupation by Mn cannot be completely neglected. From 203 to 654 K, the sample is in paramagnetic state and its average thermal expansion coefficient is $\bar{\alpha} = \Delta v/(v\Delta T) = 2.4 \times 10^{-5}$/K.

Fig.4 Temperature dependence of unit-cell volume of $Nd_2AlFe_{11}Mn_5$ compound(dash line represents phonon contribution to thermal expansion)

The temperature dependences of the extrapolated values v_p, a_p and c_p are given in Fig.3 and Fig.4, respectively. Here the signs m and p represent the unit cell parameters in the magnetic state and paramagnetic state, respectively. In terms of the deviation from the extrapolated curves from the paramagnetic to ferromagnetic (see Figs.3 and 4), we can easily obtain the uniaxial deformation λ_c, basal-plane linear deformation λ_a and volume effect ω_s (see Fig.5). From the figure, it can be seen that the linear deformation differs considerably from 1.6×10^{-3} at 103 K to around zero at 203 K. In addition, λ_c is larger than λ_a at the same temperature below 122 K. This indicates that there is much stronger spontaneous magnetostriction along the c axis than in basal plane at low temperature. The volume effect ω_s is close to zero at 203 K which is about 50 K higher than T_c. It may be due to the short-range ordering.

Fig.5 Temperature dependences of spontaneous magneto-striction deformations ω_S, λ_c and λ_a of $Nd_2AlFe_{11}Mn_5$ compound

4 Conclusions

There exists an anisotropic strong spontaneous magnetostriction in $Nd_2AlFe_{11}Mn_5$ compound and there is a negative thermal expansion coefficient of $Nd_2AlFe_{11}Mn_5$ compound in the temperature range from 122 to 203 K.

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