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Abnormal Thermal Expansion Property in Cubic $NaZn_{13}$-type $La(Fe,Al)_{13}$ Compounds

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The cubic $NaZn_{13}$-type $La(Fe,Al)_{13}$ compounds were synthesized, and their linear thermal expansion properties were investigated in the temperature range of 4.2-300K. It was found that these compounds perform abnormal thermal expansion behavior, i.e., pronounced negative thermal expansion (NTE) or zero thermal expansion (ZTE) behavior, below the Curie temperature due to magnetovolume effect (MVE). Moreover, in the $La(Fe,Al)_{13}$ compounds, the modification of coefficient of thermal expansion (CTE) as well as abnormal thermal expansion (ATE) temperature-window is achieved through optimizing the proportion of Fe and Al. Typically, the average CTE of the $LaFe_{13-x}Al_x$ compounds with x=1.8 reaches as large as $-10.47\times10^{-6}K^{-1}$ between 100 and 225K (ΔT=125K). Also, the ZTE temperature-window of the $LaFe_{13-x}Al_x$ compounds with x=2.5 and x=2.7 could be broadened to 245K (from 5 to 250K). Besides, the magnetic properties of these compounds were measured and correlated with the abnormal thermal expansion behavior. The present results highlight the potential application of such $La(Fe,Al)_{13}$ compounds with abnormal thermal expansion properties in cryogenic engineering.

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Introduction

It is well-known that materials generally expand with increasing temperature and contract with decreasing temperature. Nevertheless, there are some materials whose thermal expansion behave differently from common materials and thus feature abnormal thermal expansion (ATE) properties. Among these ATE materials, some expand with decreasing temperature and present negative thermal expansion (NTE) behavior. For the other ATE materials, they neither expand nor contract over a certain temperature range, so they show near zero thermal expansion (ZTE) properties. In recent years, the abnormal thermal expansion properties have drawn considerable attention because they could reduce thermal stress induced by rapid temperature change. Especially, in the field of aerospace, optical devices and machinery parts, thermal shock resistance would be improved by use of NTE and ZTE materials. Until now, several kinds of materials with NTE properties were discovered, such as $LiAlSiO_4$, CuO nanoparticles,[1] ZrW_2O_8,[2, 3] $PbTiO_3$-based compounds,[4] ScF_3,[5] anti-perovskite manganese nitride[6-11] and $La(Fe,Si)_{13}$-based compounds.[12] Besides, a small number of materials with ZTE properties were also studied，e.g., Invar Fe-Ni alloys, Mn_3AN, $Fe[Co(CN)_6]$, $N(CH_3)_4CuZn(CN)_4$ and YbGaGe.[13, 14] However, the practical applications of these abnormal thermal expansion materials are very limited due to their finite NTE coefficient, thermal expansion anisotropy and low mechanical strength. Among these materials shown above, although Fe-based $La(Fe,X)_{13}$ compounds are widely known as a kind of magnetic refrigeration materials,[15] they perform adjustable thermal expansion coefficient, relatively high thermal conductivity and electrical conductivity.

In our previous study, we have investigated the thermal expansion and magnetic properties of $La(Fe,X)_{13}$ compounds with different Si and Co concentration. The results show that pronounced NTE coefficient and wide NTE temperature-window can be obtained in the $LaFe_{10.5}Co_{1.0}Si_{1.5}$ compounds. [12] That is to say, appropriate control of chemical composition in the $La(Fe,X)_{13}$ compounds suggests their regulation of coefficient of negative thermal expansion (CTE) and NTE temperature-window. Based on this research, it is highly possible to obtain desired CTE for more practical application through adjusting the amount of other doped element. For the past

few years, the intermetallic compounds $La(Fe,Al)_{13}$ have been studied due to the large magnetocaloric effect (MCE) which is the consequence of itinerant electron metamagnetic transition (IEMT) and large lattice expansion during magnetic phase transition in $La(Fe,Si)_{13}$ compounds.[16] Moreover, the $La(Fe,Al)_{13}$ compounds have also attracted much attention because of their complex magnetic properties.[17] In the $La(Fe,Al)_{13}$ compounds with cubic $NaZn_{13}$-type structure (space group Fm3c), Fe atoms occupy 8b (Fe^{I}) and 96i (Fe^{II}) sites and Al atoms occupy 96i (Fe^{II}) sites, as shown in Figure 1. The competition between Fe-Al-Fe antiferromagnetic superexchange coupling and Fe-Fe ferromagnetic direct-exchange coupling is crucial for the sharp magnetic transition and excellent MCE.[16] Such a ferromagnetic (FM) state can be induced by the enhancement of the Fe-Fe distance which could be regulated through optimizing chemical composition.[17] Different Al concentration of the $LaFe_{13-x}Al_x$ compounds exhibits various magnetic properties and as a result performs diverse CTEs and NTE temperature-windows.[18] It is significant to investigate their multiple magnetic states for revealing the abnormal thermal expansion mechanism. Whereas, few reports are available about the influence of Al content on thermal expansion and relevant magnetic properties of $La(Fe,Al)_{13}$.

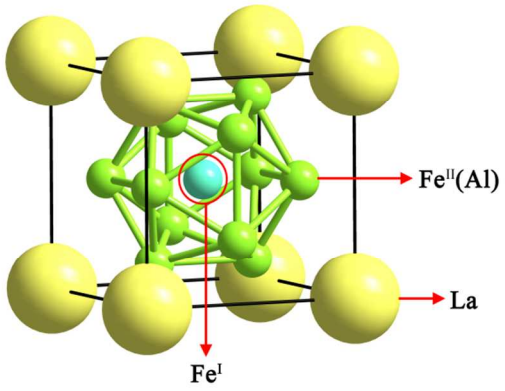

Fig. 1. Cubic $NaZn_{13}$-type crystal structure (space group Fm3c) of the $La(Fe,Al)_{13}$ compounds.

In this paper, investigations on the thermal expansion and magnetic properties with different Al concentration were performed in detail. It was found that the $La(Fe,Al)_{13}$ compounds show remarkable negative coefficient of thermal expansion and wide NTE temperature-window at low temperatures. Even, the CTE of these compounds would be considerable small at low temperatures when the amount of Al element attains to certain value.

Experimental procedure

$LaFe_{13-x}Al_x$ compounds with x=1.8, 1.9, 2.1, 2.3, 2.5 and 2.7 were synthesized by arc melting the constituent metals in a high-purity argon atmosphere. The purity of the starting elements was higher than 99.9 wt %. The ingots were remelted for four times to ensure homogeneity during melting, then sealed in an vacuum quartz tube, subsequently annealed at 900°C for 10 days, and finally quenched quickly into ice water. The crystal structure and lattice parameters were confirmed by powder X-ray diffraction (XRD) at different temperatures. The linear thermal expansion data ($\Delta L/L_{(300K)}$) were measured using a strain gage over a temperature range of 4.2-300K. Measurements of magnetization at different temperatures were performed on a physical property measurement system (PPMS).

Results and discussion

Structure

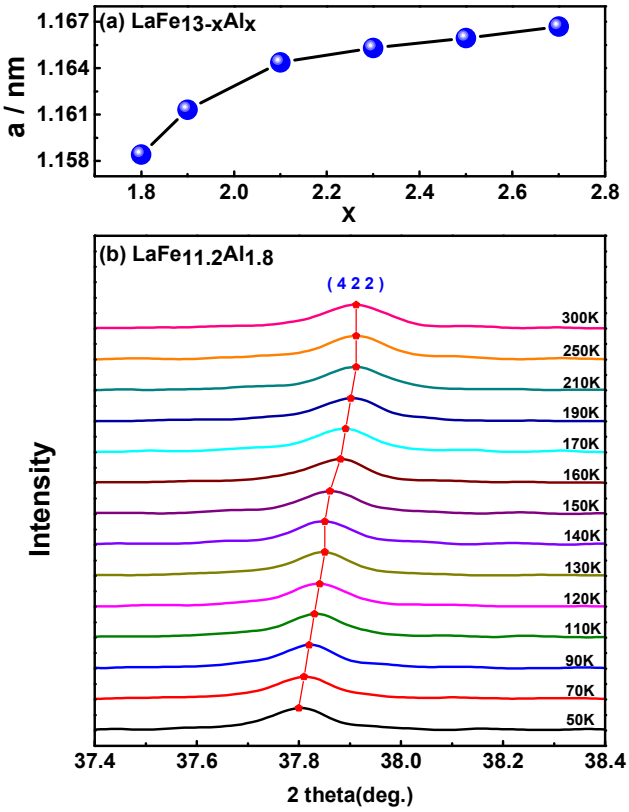

FIG. 2. (a) Crystal lattice parameters as a function of the Al concentration for samples of $LaFe_{13-x}Al_x$ (x=1.8, 1.9, 2.1, 2.3, 2.5 and 2.7) at 300K. (b) X-ray diffraction patterns of (422) peak for the $La(Fe,Al)_{13}$ compounds with x=1.8 at different temperatures.

Fig. 2(a) displays the variations of the cubic lattice parameter as a function of Al content. From this figure, the lattice parameter increases from 1.158 nm for x=1.8 to 1.167 nm for x=2.7. As expected, after increasing the amount of Al element, lattice volume becomes bigger due to larger atom radius of Al atom. It illustrates that we have successfully increased the amount of Al element. Moreover, X-ray diffraction was used to examine the temperature dependence of lattice parameter for the sample of $LaFe_{11.2}Al_{1.8}$. Fig. 2(b) shows the X-ray diffraction patterns of (4 2 2) peak for $LaFe_{11.2}Al_{1.8}$ at different temperatures. It is obvious that it maintains the cubic $NaZn_{13}$-type structure in the whole examined temperature range, and the reflections are shifted slightly to lower 2 theta angle with the decreasing test temperature from 210 to 50K. This result means that the lattice parameter increases with the decreasing temperature below 210K according to Bragg equation ($2d\sin\theta = n\lambda$), consequently its volume expands.

Thermal expansion properties

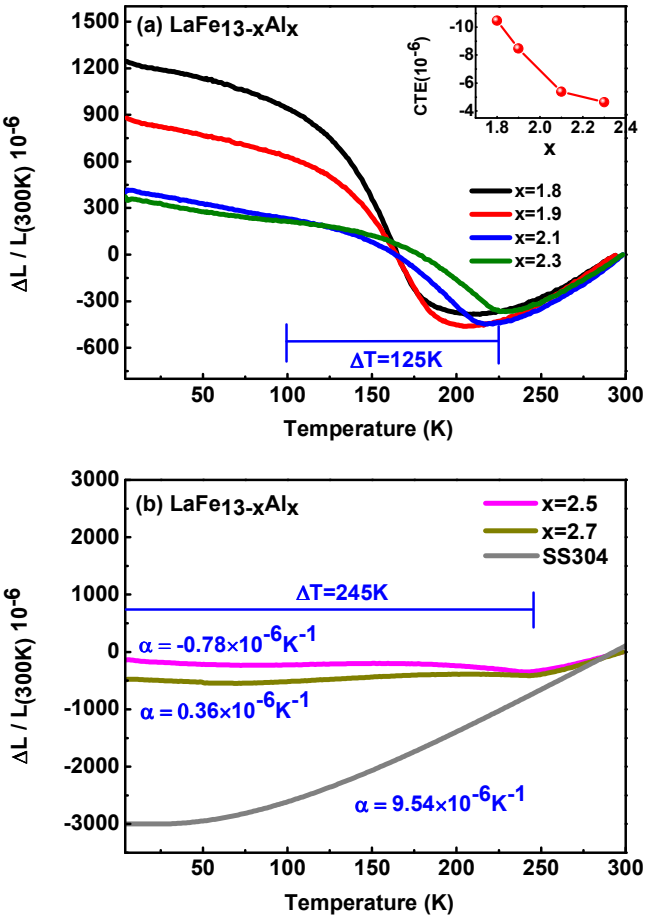

FIG. 3. (a) Temperature dependence of linear thermal expansion $\Delta L/L$ (reference temperature: 300K) from 4.2K to 300K for samples of $LaFe_{13-x}Al_x$ (x=1.8, 1.9, 2.1 and 2.3). Inset shows the average value of CTE between 100 and 225K with different Al content for samples of $LaFe_{13-x}Al_x$ (x=1.8, 1.9, 2.1 and 2.3). (b) Temperature dependence of linear thermal expansion $\Delta L/L$ (reference temperature: 300K) from 4.2K to 300K for samples of $LaFe_{13-x}Al_x$ (x=2.5, 2.7) and 304 stainless steel.

Figure 3(a) shows linear thermal expansion ($\Delta L/L$) data (reference temperature: 300K) as a function of temperature for $LaFe_{13-x}Al_x$ (x=1.8, 1.9, 2.1, and 2.3). It is apparent that the linear thermal expansion data ($\Delta L/L$) first decreases above Curie temperature (T_c), and then increases below T_c with the decreasing temperature for the samples of $LaFe_{13-x}Al_x$ (x=1.8, 1.9, 2.1, and 2.3). In detail, for the temperature range below T_c, the increase rate of $\Delta L/L$-T curve is considerable large above 100K and becomes much smaller below 100K. The average value of CTE between 100 and 225K (the $\Delta L/L$ rises quickly in this temperature region) with different Al concentration is shown in the inset of Figure 3(a). This curve presents that the absolute value of average CTE reduces with the increase of Al content, which means that pronounced NTE in $La(Fe,Al)_{13}$ compounds results from relatively low content of Al element. Particularly, the average CTE of $LaFe_{13-x}Al_x$ with x=1.8 is $-10.47\times10^{-6}K^{-1}$. Whereas for the sample of $LaFe_{13-x}Al_x$ with x=2.3, the average CTE is -4.64×10^{-6} K^{-1}. Furthermore, another important feature to be stressed is that, after a rapid increase of $\Delta L/L$, the rate of $\Delta L/L$ in the $La(Fe,Al)_{13}$ compounds is still negative at lower temperatures. It is thus not consistent with that of other materials that exhibit a NTE due to magnetovolume effect. For instance, the Ge-doped Mn3AN (A=Cu, Zn, Ga) shows positive CTE or near zero CTE after a rapid increase of $\Delta L/L$.[6] This result suggests that the NTE mechanism of $La(Fe,Al)_{13}$ compounds is different or even more complicated than that of other NTE materials. Hence, wider NTE temperature-window could be obtained due to the special performance of $\Delta L/L$ increasing rate in the $La(Fe,Al)_{13}$ compounds. Above all, it is concluded that these compounds with appropriate value of negative CTE and NTE temperature-window could be synthesized for practical application by adjusting Al concentration.

Temperature dependence of linear thermal expansion $\Delta L/L$ from 4.2K to 300K for samples of $LaFe_{13-x}Al_x$ (x=2.5, 2.7) and 304 stainless steel selected as a reference is shown in Figure 3(b). Obviously, the $\Delta L/L$ of 304 stainless steel (304SS),[19] which is regarded as one kind of classical positive thermal expansion materials, reduces with the decreasing temperature in the whole examined temperature region. Whereas, the $\Delta L/L$-T curves for the samples of $LaFe_{13-x}Al_x$ (x=2.5, 2.7) decrease above 250K, which act the same behavior as that of normal positive thermal expansion (PTE), but change slightly at lower temperatures. After calculation, the average CTEs of x=2.5 and 2.7 as well as 304SS from 4.2K to 250K (ΔT=245K) are $-0.78\times10^{-6}K^{-1}$, $0.36\times10^{-6}K^{-1}$, and $9.54\times10^{-6}K^{-1}$, respectively. The CTE value of $LaFe_{13-x}Al_x$ (x=2.5 and 2.7) is less than a tenth of that of 304SS. Moreover, the absolute value of these two CTEs are smaller than the absolute value of $-1.1\times10^{-6}K^{-1}$ in ZTE $Pb_{0.8}La_{0.2}TiO_3$.[20] Especially, the CTE value of x=2.7 is even 38.25% smaller than the value of $5.83\times10^{-7}K^{-1}$ in Mn3Zn0.93N.[21] It can be observed from above data that the NTE behavior gradually disappears with the increase of Al element and begins to show ZTE in a wide low-temperature range. In general, the ZTE behavior is obtained to form composite by combining normal PTE materials with exceptional materials showing NTE properties.[20] Nevertheless, in such composites, the mechanical strength is degraded attributing to thermal stress at interfaces or crystal boundaries caused by incongruous thermal expansion. As to $La(Fe,Al)_{13}$ ZTE materials, such mechanical problem could be improved due to the single cubic $NaZn_{13}$-type phase. It is easy to understand that the average value of CTE around zero is of great use for eliminating the hazards caused by expansion and contraction. Furthermore, these compounds exhibit a considerable wider ZTE temperature-window (ΔT=245K), which is wider than that of previously reported materials. For instance, the ZTE temperature range is ΔT=105K (298-403K) in the $Pb_{0.8}La_{0.2}TiO_3$ compounds and is ΔT=218K (12-230K) in the Mn 787 material (Mn3Cu0.5Ge0.5N).[14, 20] Such ZTE property is desired in many fields of precision engineering, including machining and processing, electronics and optics.[22]

Magnetic properties

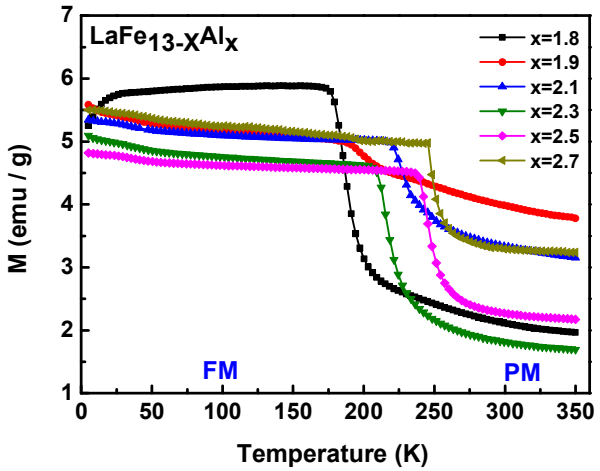

FIG. 4. Temperature dependence (5-350K) of zero-field-cooled (ZFC) magnetization in a magnetic field of 0.05T for samples of $La(Fe,Al)_{13}$ (x=1.8, 1.9, 2.1, 2.3, 2.5 and 2.7).

Previous reports have indicated that normal positive thermal expansion (PTE) is the consequence of the anharmonicity of lattice, whereas ATE is induced by magnetovolume effect (MVE) in the $La(Fe,X)_{13}$-based compounds. In order to better comprehend the mechanism of the abnormal thermal expansion, we have measured magnetic properties of the $La(Fe,Al)_{13}$ compounds. Figure 4 exhibits the temperature dependence of zero-field-cooled (ZFC) magnetization for each sample of $LaFe_{13-x}Al_x$ and each curve presents a sharp change around Curie temperature (T_c). The magnetic state is paramagnetic (PM) around room temperature and the nonzero magnetization might be attributed to the existing α-Fe phase in these $La(Fe,Al)_{13}$ compounds. Below T_c, these compounds show ferromagnetic (FM) state.[23, 24] That is to say, there exists a magnetic transition (PM-FM) around T_c. Contrasting $\Delta L/L$ data of Figure 3 with M-T curve of Figure 4, it is found that the ATE starting temperature is consistent with the magnetic phase transition temperature, i.e., magnetovolume effect (MVE) occurs. The $La(Fe,Al)_{13}$ compounds perform normal PTE behavior above T_c, but begin to show abnormal thermal expansion behavior from T_c with the decrease of temperature. When the volume expansion caused by MVE effect conquers the volume contraction due to lattice anharmonicity effect with the decreasing temperature, the materials perform NTE behavior as a whole. Similarly, the materials exhibit ZTE behavior when the lattice expansion almost equals the lattice contraction.

The Curie temperature (T_c) is calculated by taking the first derivative of magnetization and it is the corresponding temperature to the smallest value of dM/dT. Higher value of T_c means that the MVE effect occurs at higher temperatures, leading to abnormal thermal expansion behavior at higher temperatures. By the calculation, T_c moves to higher temperature with the increasing amount of Al element, which means that it needs more energy to undergo the magnetic transition. As a result, it is harder for higher Al content $La(Fe,Al)_{13}$ compounds to expand around T_c. When Al element increases (x≥2.5), the NTE disappears gradually and begins to perform ZTE behavior. Besides, higher T_c demonstrates that the $La(Fe,Al)_{13}$ compounds with higher Al content present wider ATE temperature-window. In particular, the T_c of $LaFe_{13-x}Al_x$ with x=2.3 and x=1.8 is 216K and 185K, respectively, which means that the NTE temperature-window of the former is 31K wider than the latter. Previous studies [25] on the $La(Fe,Si)_{13}$-based compounds point out that Fe-Fe distance is a significant factor for influencing T_c. When increasing Al content, the Fe-Fe distance becomes larger, resulting in a stronger Fe-Fe exchange interaction, then consequently moving T_c to a higher temperature. These results prove that it is feasible to control ATE temperature-window of these compounds through optimizing chemical component, such as adding Al element. Without doubt, such optimization makes these abnormal thermal expansion compounds to be a promising candidate for broader application in the temperature sensitive equipments and devices.

Conclusion

In conclusion, we have investigated the effect of Al element on the CTE and abnormal thermal expansion temperature-window in the $La(Fe,Al)_{13}$ compounds with proper substitution of Al for Fe. Notably, the average CTE of the $LaFe_{13-x}Al_x$ with x=1.8 reaches as large as $-10.47\times10^{-6}K^{-1}$, whereas for $LaFe_{13-x}Al_x$ with x=2.3, the average CTE is $-4.64\times10^{-6}K^{-1}$ from 100 K to 225K. For the sample of $LaFe_{13-X}Al_X$ with x=2.5, its average CTE is $-0.78\times10^{-6}K^{-1}$, which is very small for causing volume expansion and contraction. The magnetic analysis results reveal that these $La(Fe,Al)_{13}$ compounds with higher Al content present wider abnormal negative temperature-window. Therefore, we believe that the CTE and abnormal thermal expansion temperature-window could be adjusted by means of doping Al element for practical use, especially for temperature sensitive equipments and devices.

Acknowledgements

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