The critical role of spin rotation in the giant magnetostriction of $\text{La}(\text{Fe},\text{Al})_{13}$

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ABSTRACT As an efficient converter between electromagnetic and mechanical energies, magnetostriction is an intriguing property for not only fundamental studies but also technological applications. However, the understanding of its microscopic origin remains challenging, which is critical for the development of magnetostriction materials. Here, the critical role of spin rotation in the giant magnetostriction of $\text{La}(\text{Fe},\text{Al})_{13}$ is first revealed by the *in-situ* magnetic and temperature field of neutron powder diffraction. The giant magnetostriction originates from magnetic-field-driven spin moment rotation of canting structure, in which the sharp increase of ferromagnetic component causes the elongation of icosahedron inside of lattice. Furthermore, it is the first time to reveal the accurate canting antiferromagnetic structure in $\text{La}(\text{Fe},\text{Al})_{13}$. The present study provides a new strategy, i.e., the spin rotation, for exploring new magnetostriction functional materials.

Keywords: magnetostriction, magnetic-field-induced spin rotation, magnetic structure, neutron powder diffraction

INTRODUCTION

Magnetostriction, a strain induced by magnetic field, is one of the frontier topics of advanced functional materials, to which much attention has been paid due to its unique role in various applications [1–11]. Magnetostrictive materials have been used as converters of electromagnetic energy into mechanical energy, such as actuators, motors, positioning devices, and energy har-

vesting [12,13]. In order to meet the actual requirement, more applicable magnetostrictive materials need to be developed. After the discovery of the magnetostrictive effect in iron by Joule in 1842 [14], a great progress in the discovery of new magnetostriction materials has been made, such as rare-earth metals, Laves phase alloys [15,16], Fe-Ga alloys [10,17–19], and Ni-Mn-Ga alloys [20,21].

Magnetostriction is a very complex phenomenon [1]. For example, the tetragonal distortion of the matrix induced by nanoheterogeneities causes large magnetostriction in Fe-Ga alloys [10,17–19], the magnetic-field-controlled twin boundary motion induces large strain in Ni-Mn-Ga alloy [20,21], and the magnetic domain rotation results in giant magnetostriction in Laves phase alloys [15,16]. The phenomenological theory of magnetostriction can explain the change of ferromagnetic morphology from the perspective of macro deformation, but it cannot explain the intrinsic physical mechanism of magnetostriction [22]. It is demanded to study the magnetostriction from the microscopic level, such as crystal structure, bond length and atomic magnetic moment, so as to guide the exploration of magnetostriction materials. However, the origin of magnetostriction remains a mystery, which also hinders the design of new magnetostriction materials.

It is well known that magnetostriction is the change of lattice caused by the variation of magnetic field. Actually, due to the strong coupling between spin and lattice de-

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degrees of freedom, the modulation of lattice with the application of external field is generally influenced by such coupling. Thus, to better understand the mechanism of magnetostriction, the best way is to start with revealing spin lattice coupling, especially studying the response between lattice and spin under the external field.

Here, the origin of the giant magnetostriction property of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ is first revealed by the *in-situ* magnetic and temperature field of neutron powder diffraction (NPD) and macroscopic magnetic measurements. The magnetostriction of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ originates from the magnetic-field-driven spin moment rotation of canting structure. Interestingly, there is a strong correlation between lattice and the angle of spin moment. Furthermore, it is the first time to reveal the canting antiferromagnetic (AFM) structure in $\text{La}(\text{Fe},\text{Al})_{13}$.

EXPERIMENTAL SECTION

The samples of single phase $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ and $\text{La}(\text{Fe}_{11.3}\text{Al}_{1.7})$ were prepared by arc melting under a high purity argon atmosphere. After melting, the samples were annealed in a vacuum-sealed quartz tube at 1223 K for 15 days, and then quickly cooled to room temperature in ice water. The temperature and magnetic field dependence of macroscopic magnetism of $\text{La}(\text{Fe},\text{Al})_{13}$ was measured by a physical property measurement system (PPMS) of Quantum Design. The variable magnetic field and temperature field measurements of NPD with wavelengths of 2.08 Å were collected in the BT-1 neutron powder diffractometer at NIST Center for Neutron Research (NCNR). The magnetic structure refinements for all NPD data were analyzed by FULLPROF software. SARAH and BASIREPS in FULLPROF were utilized for the magnetic representational analysis.

RESULTS AND DISCUSSION

Due to the positive mixing enthalpy for the binary system of La-Fe, the composition of LaFe_{13} does not exist [23–25]. However, due to the strong chemical affinity of La-Al, the partial substitution of Al for Fe can lower the heat of formation of La-Fe, so the cubic $\text{La}(\text{Fe}_{13-x}\text{Al}_x)$ compounds can be stabilized in some regions of x . As previously reported, $\text{La}(\text{Fe}_{13-x}\text{Al}_x)$ compounds can only be stabilized in the solution range of $1.04 \leq x \leq 7.02$, in which three magnetic states occur, i.e., AFM, ferromagnetic (FM), and micromagnetic one [26]. It has been known that the $\text{La}(\text{Fe},\text{Al})_{13}$ -based compounds exhibit intriguing magnetic-related properties, such as magnetostriction [27], magnetovolume [28,29], magnetocaloricity [30–32], and magnetoresistance [33], due to the

complex magnetism. In this study, two compositions of $\text{La}(\text{Fe}_{13-x}\text{Al}_x)$ ($x = 1.5$ and 1.7) at the magnetic phase boundary were prepared by an arc melting. The $\text{La}(\text{Fe}_{13-x}\text{Al}_x)$ ($x = 1.5$ and 1.7) compounds maintain in a single phase with a cubic NaZn_{13} structure (space group: $Fm-3c$) over the whole temperature range. There are three Wyckoff sites in $\text{La}(\text{Fe},\text{Al})_{13}$, i.e., La(8a) (1/4, 1/4, 1/4), Fe1(8b) (0, 0, 0), and Fe2/Al(96i) (0, y , z). As shown in Fig. 1a, one central Fe1(8b) atom and twelve surrounded Fe2(96i) atoms form an icosahedral cluster. If taking the icosahedron as one Fe unit, the crystal structure of $\text{La}(\text{Fe},\text{Al})_{13}$ can be simplified to a simple CsCl-type structure [24,34].

The variable magnetic field NPD from 0 to 5 T at $T = 100$ K was measured to study the magnetostriction property. Fig. 1b shows the magnetic field (H) dependence of lattice parameter (a) for $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$. Intriguingly, the unit cell of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ expands sharply by loading magnetic field. A giant isotropic magnetostriction (λ) of 2527 ppm calculated by $(a_{5T} - a_{0T})/a_{0T}$ can be observed at $T = 100$ K and $H = 5$ T, which is comparable to the previous macroscopic strain gauge measurement [35]. As a comparison, the magnetostriction of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ is even larger than that of the prototype Terfenol-D alloys of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_{1.9}$ ($\lambda = 1000\text{--}2000$ ppm) [15,16] and comparable to that of the FeRh alloys ($\lambda = 2733$ ppm) [36]. To study the detailed behavior of the magnetic-field-induced lattice strain, the interatomic distances between different Fe atoms of icosahedron are extracted from the NPD patterns (Fig. 1c). Obviously, the nearest interatomic distance, $d^1_{\text{Fe1-Fe2}}$, has a similar tendency with the a , which expands with increasing magnetic field and nearly saturates at 3 T. Therefore, the giant magnetostriction mainly comes from the magnetic-field-induced expansion of icosahedron. This result is related to the shortest Fe1–Fe2 distance, which plays a critical role in the magnetic exchange interaction [24]. Due to the expansion of icosahedron, some of the interatomic distances of Fe2–Fe2 increase (d^2), or decrease (d^3).

The temperature dependence of magnetization for $x = 1.5$ and 1.7 was measured by macroscopic magnetic measurements at a magnetic field of 0.1 T (Fig. 2a). Obviously, $\text{La}(\text{Fe}_{11.3}\text{Al}_{1.7})$ shows a simple ferromagnetic behavior, but when the aluminum concentration decreases slightly to $x = 1.5$, $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ performs an AFM-like behavior. In this study, the composition of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ is chosen as the main research object. The isothermal magnetization of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ at selected temperatures has been measured (Fig. 2b and Fig. S1). When the magnetic field is below 2 T, the magnetization curves

Figure 1 (a) The crystal structure of $\text{La}(\text{Fe},\text{Al})_{13}$ compounds. One Fe_1 atom is surrounded by twelve Fe_2/Al atoms, forming an icosahedron. (b) The giant magnetostriction property of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$. The magnetic field dependence of a at $T = 100$ K. (c) Magnetic field dependence of Fe-Fe distances for $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ at $T = 100$ K. The d^1 , d^2 and d^3 are marked in (a).

Figure 2 The macroscopic magnetism of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ as a function of magnetic field and temperature. (a) Temperature dependence of magnetization (FC) at $H = 0.1$ T for the AFM $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ with a comparison of the FM $\text{La}(\text{Fe}_{11.3}\text{Al}_{1.7})$. (b) Isothermal magnetization ($M-H$) of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ at $H = 0-5$ T and selected temperatures.

keep linear change without hysteresis, which indicates that the spin state of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ keeps in an AFM-like behavior at low field. However, with increasing magnetic field, a magnetic-field-induced metamagnetic transformation from the AFM-like state to the FM-like one takes place. The macroscopic magnetism of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ in

the current magnetization curves is consistent with the previous macroscopic magnetic measurement results [37]. It should be noted that when we observe the hysteresis loop carefully, a small coercive field of ~ 0.05 T can be found at $T = 5$ K, which disappears gradually with increasing temperature (Fig. S2). This means that the

magnetic state of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ is not a simple AFM structure, but a weak ferromagnetism remains.

To study the origin of giant magnetostriction in $\text{La}(\text{Fe}, \text{Al})_{13}$, the variable magnetic field NPD was analyzed in detail (Fig. 3). Firstly, it needs to be noted that the magnetic structure of $\text{La}(\text{Fe}, \text{Al})_{13}$ was ever determined to be AFM in early 1986, which was widely used [25,37]. The central Fe1 spin parallels to the surrounded twelve Fe2 spins, forming one Fe unit. The Fe units are FM coupling within a layer, but previously assumed to be AFM coupling between the layers (Fig. 4a). As shown in Fig. 3a and Fig. S3, it is observed that some magnetic peaks increase with increasing magnetic field, while others decrease simultaneously. Such phenomenon indicates that the magnetic structure of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ should be composed of two components, which cannot be simply explained by the previously assumed AFM structure. Since a small ferromagnetic signal can be found in $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$, the FM component is added into the AFM structure to refine the NPD data. The NPD data at all magnetic fields can be fitted well by the present proposed model (Fig. 3b). As shown in Fig. 4b, $\text{La}(\text{Fe}, \text{Al})_{13}$ exhibits a complex canting magnetic structure, which consists of two components of AFM and FM. The $M_{\parallel}$ and $M_{\perp}$ are used to represent the magnetic components of canting state in the parallel (the FM component) and perpendicular (the AFM component) directions, respectively.

To clearly distinguish the magnetic Bragg reflections from different components, the NPD patterns with different magnetic structures were simulated (Fig. S4). Obviously, the magnetic peaks from the FM component and AFM one are separated, which is very conducive to the analysis of magnetic structure. Due to the fact of a small ferromagnetic component, it is not easy to observe the

peaks from the FM component. That is why the ferromagnetic component was often ignored at zero magnetic field in the previous studies. Intriguingly, with increasing magnetic field at $T = 100$ K, the peaks of FM component are much enhanced. The coexistence of the FM and AFM component peaks proves the correctness of the present canting model. It is worth noting that both FM and AFM components exist in a single-phase canting state, rather than two separated phases, and the corresponding discussions are shown in the Supplementary information (Figs S5–S7). To the best of our knowledge, it is the first time to reveal the canting structure in $\text{La}(\text{Fe}, \text{Al})_{13}$. The detailed magnetic structure at different fields can be refined by the NPD data. As depicted in Fig. 4b–d, it is intriguing to observe a continuous rotation of spins by magnetic field. With increasing magnetic field, the opposite spins gradually turn to the same direction. As a result, the AFM component decreases (faint yellow), while the FM one simultaneously increases (light grey). The magnetic structure finally changes to FM structure when loading enough magnetic field.

Fig. 5a shows the magnetic field evolution of the angle (θ) of canting spins and the corresponding FM and AFM components at 100 K. The spin moment of Fe atom almost keeps constant ($|M_{\text{Total}}| = \sqrt{(M_{\parallel})^2 + (M_{\perp})^2} = 1.47 \pm 0.02 \mu_{\text{B}}$) at various magnetic fields (Fig. 5b), which means that the magnitude of total magnetic moment is not affected. However, the spin moment of canting structure is rotated by magnetic field (Fig. 5a). With increasing magnetic field, the angle θ continuously decreases. If the angle θ is close to 90° , it is in the AFM dominating state; however, as the angle θ is close to 0° , it is in the FM dominating state. Correspondingly, the $M_{\parallel}$ and $M_{\perp}$ change oppositely (Fig. 5a). At an intermediate field, one

Figure 3 (a) The magnetic field dependence of NPD patterns at $T = 100$ K. The dotted boxes highlight the magnetic Bragg reflections for the FM component ($M_{\parallel}$) and the AFM one ($M_{\perp}$). (b) Magnetic structure refinements of NPD patterns with a wavelength of $2.08 \text{ \AA}$ for $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ at $T = 100$ K and $H = 1.4$ T. The magnetic Bragg peaks are fitted by only one single-phase canting state. The inset shows the enlarged region.

Figure 4 The spin rotation of $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ as a function of magnetic field. (a) The previously assumed AFM structure in $\text{La}(\text{Fe},\text{Al})_{13}$. (b–d) The spin rotation in the canting structure from the AFM-dominated one to the FM one with increasing magnetic field. There are two magnetic vectors in the canting magnetic structure, i.e., the AFM ($M_{\perp}$) and FM ($M_{\parallel}$) components, which is determined by the angle of θ .

can observe the coexistence of FM and AFM components such as at $H = 1.4$ T (Fig. 3a). As shown in Fig. 5c, an important fact can be observed that a strong linear correlation between a and θ , which directly proves that the spin rotation results in the lattice expansion. Due to the spin rotation, the FM component of spin and the lattice has a similar evolution tendency as a function of magnetic field (Fig. 1b and Fig. 5a). It suggests that the giant magnetostriction is closely related to the FM component of Fe spin, which can be evidenced by the direct spin-lattice coupling between $M_{\parallel}$ and a (Fig. 5d). The correlation can be described quantitatively by the equation of $a = a_0 + k \cdot M_{\parallel}$ ($a_0 = 11.5819(18)$ Å, $k = 0.0282(15)$ Å μ_{B}^{-1}). Therefore, the origin of giant magnetostriction in $\text{La}(\text{Fe},\text{Al})_{13}$ is related to the sharp increase of FM component, which is caused by the rotation of canting magnetic spins. The nature of magnetic-field-induced rotation of magnetic spins in $\text{La}(\text{Fe},\text{Al})_{13}$ shows an interesting behavior similar to the role of electric-field-driven polarization

rotation in the high performance piezoelectrics [38]. It is very important to reveal the common nature that the lattice can be expanded by rotation of either spin in magnetics or polarization in ferroelectrics at external field, which correspondingly triggers high performances of magnetostriction or piezoelectricity.

It is noteworthy that the origin of magnetostriction of present $\text{La}(\text{Fe},\text{Al})_{13}$ is different from that of $\text{La}(\text{Fe},\text{Si})_{13}$, which is caused by the itinerant electron metamagnetic transition, i.e., the PM-to-FM transition [27,39]. In previous studies, it is believed that the metamagnetic transformation in $\text{La}(\text{Fe},\text{Al})_{13}$ is the AFM-to-FM transition [26,37]. In fact, the previous proposed metamagnetic transformation is just the rotation of single-phase canting magnetic state, which results from the change of AFM and FM components. The spin rotation may be the essential reason for the metamagnetic transformation of most materials. For example, the AFM-to-FM transition caused by the field-induced spin reorientation has also

Figure 5 (a) The magnetic field evolution of θ of canting spins and the corresponding magnetic moments of FM component ($M_{||}$) and AFM one ($M_{\perp}$). (b) The total moment of Fe spins at 100 K as a function of magnetic field. (c) A strong spin-lattice coupling between a and θ of canting spins. (d) a as a function of FM component moment at various magnetic fields at 100 K.

been found in EuFe_2As_2 [40]. The present understanding in the magnetostriction mechanism is beyond the phenomenological description for magnetostriction, which will be helpful for the design of high-performance magnetostrictive materials in the future. In order to obtain high-performance magnetostrictive materials, it may be an effective pathway to obtain the unique magnetic structure which enables spin rotation smoothly driven by magnetic field.

CONCLUSIONS

In summary, the origin of giant magnetostriction ($\lambda = 2527$ ppm) in $\text{La}(\text{Fe},\text{Al})_{13}$ is revealed by the direct experimental evidence for the first time. The magnetic structure of $\text{La}(\text{Fe},\text{Al})_{13}$ is not a simple AFM structure, but the canting antiferromagnet which performs weak ferromagnetism. The magnetic-field-triggered rotation of canting magnetic structure makes the AFM component transform to the FM one, which results in the expansion of icosahedron inside the lattice, so that the giant magnetostriction is induced. This study proves that the spin rotation may be a new strategy for obtaining large magnetostriction, which is helpful for exploring new mag-

netostriction materials.

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- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

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自旋旋转在 La(Fe,Al)_{13} 超磁致伸缩中的关键作用

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摘要 磁致伸缩可作为电磁能和机械能之间的高效转换途径, 是基础研究以及技术应用等方面重要的材料性能。然而, 在其微观成因的理解方面仍然存在挑战, 这对磁致伸缩材料的发展非常重要。本文利用原位磁场和温度场下的粉末中子衍射技术首次揭示了自旋旋转对 La(Fe,Al)_{13} 超磁致伸缩的关键作用。 La(Fe,Al)_{13} 超磁致伸缩性能是由磁场驱动的倾斜结构磁矩旋转引起的, 其中铁磁成分的急剧增加促使晶格内部二十面体伸长, 进而产生巨大的磁致伸缩。此外, 本文揭示了 La(Fe,Al)_{13} 精确的倾斜磁结构特征。本研究提供了一种通过磁场诱导自旋旋转途径探索新型磁致伸缩功能材料的策略。