Site occupancy and magnetic properties of Al-substituted M-type strontium hexaferrite

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We use first-principles total-energy calculations based on density functional theory to study the site occupancy and magnetic properties of Al-substituted M-type strontium hexaferrite SrFe_{12−x}Al_{x}O_{19} with x = 0.5 and x = 1.0. We find that the non-magnetic Al^{3+} ions preferentially replace Fe^{3+} ions at two of the majority spin sites, 2a and 12k, eliminating their positive contribution to the total magnetization causing the saturation magnetization $M_s$ to be reduced as Al concentration $x$ is increased. Our formation probability analysis further provides the explanation for increased magnetic anisotropy field when the fraction of Al is increased. Although Al^{3+} ions preferentially occupy the 2a sites at a low temperature, the occupation probability of the 12k site increases with the rise of the temperature. At a typical annealing temperature (> 700$°$C) Al^{3+} ions are much more likely to occupy the 12k site than the 2a site. Although this causes the magnetocrystalline anisotropy $K_1$ to be reduced slightly, the reduction in $M_s$ is much more significant. Their combined effect causes the anisotropy field $H_a$ to increase as the fraction of Al is increased, consistent with recent experimental measurements.

I. INTRODUCTION

Strontium hexaferrite, SrFe_{12}O_{19} (SFO) is one of the most commonly used materials for permanent magnets, magnetic recording and data storage, and components in electrical devices operating at microwave/GHz frequencies, due to its high Curie temperature, large saturation magnetization, excellent chemical stability and low manufacturing cost [1–5]. However, in comparison with Nd-Fe-B and magnet, the coercivity of the SFO is low and presents a significant limitation in its application. Therefore, enhancement of the coercivity is an important research topic for the strontium hexaferrite.

In order to tailor the magnetic properties such as magnetization and coercivity, various cation substitutions in the M-type hexaferrites have been investigated. For example, the substitution of La [6, 7], Sm [8], Pr [9] and Nd [10] in the SFO increased coercivity moderately while the substitution of Zn-Nb [11], Zn-Sn [12, 14] and Sn-Mg [14] decreased coercivity. However, the coercivity of the M-type hexaferrites is not increased significantly by these cation substitutions, and is still much smaller than that of Nd-Fe-B magnet [15].

Al substitution in the M-type hexaferrite has been more effective in enhancing coercivity [16–20]. Particularly, Wang et al synthesized Al-doped SFO SrFe_{12−x}Al_{x}O_{19} (SFAO) with Al content of $x = 0 – 4$ using glycinitrate method and subsequent annealing in a temperature over 700$°$C obtaining the largest coercivity of 17.570 kOe, which is much larger than that of SFO (5.356 kOe) and exceeds even the coercivity of the Nd$_2$Fe$_{17}$B (15.072 kOe) [1]. Wang and co-workers also observed that the coercivity of the SFAO increases with increasing Al concentration at a fixed annealing temperature. These results call for a systematic understanding, from first principles, of why certain combinations of dopants lead to particular results. This theoretical understanding will be essential in systematically tailoring the properties of SFO.

There have been several previous first-principles investigations of SFO. Fang et al investigated the electronic structure of SFO using density-functional theory (DFT)
II. METHODS

SFO has a hexagonal magnetoplumbite crystal structure that belongs to P6\textsubscript{3}/mmc space group. Fig. 1 shows a unit cell of SFO used in the present work that contains 64 atoms of two formula units. Magnetism in SFO arises from Fe\textsuperscript{3+} ions occupying five crystallographically inequivalent sites in the unit cell, three octahedral sites (2\textit{a}, 12\textit{k}, and 4\textit{f}2), one tetrahedral site (4\textit{f}1), and one trigonal bipyramidal site (2\textit{b}) as represented by the polyhedra in Fig. 1(a). SFO is also a ferrimagnetic material that has 16 Fe\textsuperscript{3+} ions with spins in the majority direction (2\textit{a}, 2\textit{b}, and 12\textit{k} sites) and 8 Fe\textsuperscript{3+} ions with spins in the minority direction (4\textit{f}1 and 4\textit{f}2 sites) as indicated by the arrows in Fig. 1(b).

Total energies and forces were calculated using DFT with projector augmented wave (PAW) potentials as implemented in VASP \cite{25, 26}. All calculations were spin polarized according to the ferrimagnetic ordering of Fe spins as first proposed by Gorter \cite{21, 27}. A plane-wave energy cutoff of 520 eV was used both for pure SFO and Al-substituted SFO. Reciprocal space was sampled with a 7 × 7 × 1 Monkhorst-Pack mesh \cite{28} with a Fermi-level smearing of 0.2 eV applied through the Methfessel-Paxton method \cite{29}. We performed relaxation of the electronic degrees of freedom until the change in free energy and the band structure energy was less than 10\textsuperscript{−7} eV. We performed geometric optimizations to relax the positions of ions and cell shape until the change in total energy between two ionic steps was less than 10\textsuperscript{−4} eV. Electron exchange and correlation was treated with the generalized gradient approximation (GGA) as parameterized by the Perdew-Burke-Ernzerhof (PBE) scheme \cite{30}. To improve the description of localized Fe 3d electrons, we employed the GGA+U method in the simplified rotationally invariant approach described by Dudarev et al. \cite{31}. This method requires an effective $U$ value ($U_{\text{eff}}$) equal to the difference between the Hubbard parameter $U$ and the exchange parameter $J$. We chose $U_{\text{eff}}$ equal to 3.7 eV for Fe based on the previous result \cite{14}.

III. RESULTS AND DISCUSSION

The substitution of Fe\textsuperscript{3+} ions by Al\textsuperscript{3+} ions considerably affects the unit cell parameters. We have calculated the lattice parameters of pure and Al-substituted SFO by relaxing ionic positions as well as the volume and shape of the unit cell. In all cases the final unit cell was found to remain hexagonal. In the case of pure SFO, the lattice parameters $a$ and $c$ were found to be 5.93 Å and 23.21 Å in good agreement with the experimental values of $a = 5.88$ Å and $c = 23.04$ Å, respectively \cite{19, 32}: the deviation between the experimental and the theoretical values is less than 1%. In the case of $x = 0.5$ in SRO, the lattice parameters $a$ and $c$ were calculated to be 5.92 Å and 23.16 Å respectively, while the volume of the unit cell was reduced by 0.61%. For
FIG. 2. (color online) Comparison of calculated and experimental (Ref. [19]) volume of the unit cell of SrFe$_{12-x}$Al$_x$O$_{19}$ as a function of the fraction of Al $x$.

$x = 1.0$, $a = 5.91$ Å and $c = 23.04$ Å were found, and reduction in the unit cell volume was 2.51%. Fig. 2 shows that the reduction of unit cell volume predicted by our DFT calculation is consistent with the experimental results [1, 19].

We investigated the site preference of Al substituting Fe in SrFe$_{12-x}$Al$_x$O$_{19}$ for (i) $x = 0.5$ and, (ii) $x = 1.0$. The $x = 0.5$ case corresponds to the condition where one Al atom is substituted in the unit cell, while two Al atoms were substituted in the case of $x = 1.0$ as shown Fig. 3. To determine the site preference of the substituted Al atoms, the substitution energy of configuration $i$ was calculated using the following expression:

$$E_{\text{sub}}(i) = E(\text{SFAO}(i)) - E(\text{SFO}) - \sum_\alpha n_\alpha \epsilon(\alpha)$$ (1)

where $E(\text{SFAO}(i))$ is the total energy per unit cell at 0 K for SFAO in configuration $i$ while $E(\text{SFO})$ is the total energy per unit cell at 0 K for SFO. $\epsilon(\alpha)$ is the total energy per atom for element $\alpha$ ($\alpha = \text{Al, Fe}$) at 0 K in its most stable crystal structure. $n_\alpha$ is the number of atoms of type $\alpha$ added: if two atoms are added then $n_\alpha = +2$ while $n_\alpha = -1$ when one atom is removed. The configuration with the lowest $E_{\text{sub}}$ is concluded to be the ground state configuration, and the corresponding substitution site is the preferred site of Al atoms at 0 K.

To understand the site preference of the substituted Al$^{3+}$ ions at higher temperatures, we compute the formation probability of configuration $i$ using the Maxwell-Boltzmann statistical distribution [33]:

$$P_i = \frac{g_i \exp(-\Delta G_i/k_B T)}{\sum_j g_j \exp(-\Delta G_j/k_B T)}$$ (2)

where $g_i$ is the multiplicity of configuration $i$ (number of equivalent configurations) and

$$\Delta G_i = \Delta E_{\text{sub}}(i) + P \Delta V_i - T \Delta S_i$$ (3)

is the change of the free energy of configuration $i$ relative to that of the ground state configuration: $\Delta E_{\text{sub}}(i)$, $\Delta V_i$, and $\Delta S_i$ are the substitution energy change, volume change, entropy change for configuration $i$; $P$ and $k_B$ are the pressure and Boltzmann constant.

For the $x = 0.5$ concentration, one Al atom is substituted at one of the 24 Fe sites of the unit cell as shown in Fig. 3(a). The application of crystallographic symmetry operations shows that many of these Fe sites are equivalent and leaves only five inequivalent structures. We label these inequivalent configurations using the crystallographic name of the Fe site: [2$a$], [2$b$], [4$f_1$], [4$f_2$], and [12$k$]. These structures were created by substituting one Al atom to the respective Fe site of a SFO unit cell and performing full optimization of the unit cell shape and volume, and ionic positions.

Table I lists the results of our calculation for all five inequivalent configurations in the order of increasing substitution energy. The lowest $E_{\text{sub}}$ is found for configuration [2$a$] shown in Fig. 3(a). We can conclude that at 0 K the most preferred site for the substituted Al atom is the 2$a$ site. We used Eq. (2) to compute the
TABLE I. Five inequivalent configurations of SrFe\textsubscript{12-x}Al\textsubscript{x}O\textsubscript{19} with \(x = 0.5\). \(g\) is the multiplicity of the configuration. \(E_{\text{sub}}\) is the substitution energy of the SFAO. The total magnetic moment \((m_{\text{tot}})\) and its change with respect to SFO \((\Delta m_{\text{tot}})\) are also given. All values are for a double formula unit cell containing 64 atoms. Energies are in eV while magnetic moments are in \(\mu_B\).

| Config | \(g\) | \(E_{\text{sub}}\) | \(m_{\text{tot}}\) | \(\Delta m_{\text{tot}}\) |
|--------|------|----------------|----------------|----------------|
| [2a]   | 2    | -6.04          | 35             | -5             |
| [12k]  | 12   | -6.00          | 35             | -5             |
| [4f\textsubscript{2}] | 4    | -5.63          | 45             | +5             |
| [2b]   | 2    | -5.60          | 35             | -5             |
| [4f\textsubscript{1}] | 4    | -5.57          | 45             | +5             |

FIG. 4. (color online) Temperature dependence of the formation probability of different configurations of SrFe\textsubscript{12-x}Al\textsubscript{x}O\textsubscript{19} with \(x = 0.5\). The configurations with negligible probability are not shown.

probability to form each configuration as a function of temperature. Since the volume change among different configurations is very small (less than 0.1\(\AA\)), we can safely regard \(P\Delta V\) term to be negligible (in the order of \(10^{-7}\) eV at the standard pressure of 1 atm) compared to the \(\Delta E_{\text{sub}}(i)\) term in Eq. (3). The entropy change \(\Delta S\) has a configurational part, \(\Delta S_{\text{c}}\), and a vibrational part, \(\Delta S_{\text{vib}}\). For binary substitutional alloys such as the present system, \(\Delta S_{\text{vib}}\) is around 0.1-0.2 k\(B\)/atom, and \(\Delta S_{\text{c}}\) is 0.1732 k\(B\)/atom. Therefore, we set \(\Delta S = 0.3732\) k\(B\)/atom.

Fig. 4 displays the temperature dependence of the formation probability of different configurations of SrFe\textsubscript{12-x}Al\textsubscript{x}O\textsubscript{19} with \(x = 0.5\). The doped Al\textsuperscript{3+} ions mainly replace Fe\textsuperscript{3+} ions from the 2a and the 12k sites. The formation probabilities of [2b], [4f\textsubscript{1}] and [4f\textsubscript{2}] are negligible and not shown in Fig. 4. The probability that the doped Al\textsuperscript{3+} ion replaces Fe\textsuperscript{3+} ion from the 2a site is maximum at 0 K and it falls as temperature increases, while the occupancy of Al\textsuperscript{3+} at the 12k site rises with temperature. The two curves cross at \(T \sim 220\) K. At a typical annealing temperature of 1000 K for SFAO, the site occupation probability of the site 2a and 12k is 0.196 and 0.798, respectively. Thus, during the annealing process of the synthesis of the SFAO the doped Al\textsuperscript{3+} ions are more likely to replace Fe\textsuperscript{3+} ions from the 12k site than the 2a site despite of higher substitution energy.

For the \(x = 1.0\) concentration, two Al atoms are substituted at two of the 24 Fe sites of the unit cell as shown in Fig. 3(b). These Fe sites have more than one equivalent site. Substitution of Al atoms breaks the symmetry of the equivalent sites of pure SFO. Out of all \(C(24, 2) = 276\) possible structures, many of the structures are crystallographically equivalent. On applying crystallographic symmetry operations, the number of inequivalent structures reduces to 40. We label these inequivalent configurations using the convention of \([\text{site for the first Al}),(\text{site for the second Al})\] (unique index). For example, when two Al atoms are substituted at the 2a and 12k sites, there are 2 inequivalent configurations, which are labeled as [2a, 12k].1 and [2a, 12k].2. These structures are fully optimized and their substitution energies are calculated using Eq. (1). When there are more than one inequivalent configuration, we assign the unique index in the order of increasing \(E_{\text{sub}}\).

Table II lists the ten lowest energy configurations of SrFe\textsubscript{12-x}Al\textsubscript{x}O\textsubscript{19} with \(x = 1.0\). The configuration [2a, 2a] where two Al\textsuperscript{3+} ions replace Fe\textsuperscript{3+} ions from two 2a sites has the lowest \(E_{\text{sub}}\), and it is the most energetically favorable configuration at 0 K. To investigate the site occupation at nonzero temperatures we compute the formation probability of each configuration using Eq. (2). Similar to the previous case the volume change among different configurations is very small (less than 0.7\(\AA\)) and we can safely ignore the \(P\Delta V\) term. The entropy term is calculated in the same way as the \(x = 0.5\) case.

Fig. 5 shows the variation of the formation probability with respect to temperature for two of the ten configurations.

TABLE II. Ten lowest energy inequivalent configurations of SrFe\textsubscript{12-x}Al\textsubscript{x}O\textsubscript{19} with \(x = 1.0\). \(g\) is the multiplicity of the configuration. \(E_{\text{sub}}\) is the substitution energy per Al atom. The total magnetic moment \((m_{\text{tot}})\) and its change with respect to SFO \((\Delta m_{\text{tot}})\) are also given. All values are for a double formula unit cell containing 64 atoms. Energies are in eV while moments are in \(\mu_B\).

| Config | \(g\) | \(E_{\text{sub}}\) | \(m_{\text{tot}}\) | \(\Delta m_{\text{tot}}\) |
|--------|------|----------------|----------------|----------------|
| [2a, 2a] | 1    | -6.056         | 30             | -10            |
| [2a, 12k].1 | 12   | -6.054         | 30             | -10            |
| [2a, 12k].2 | 12   | -6.041         | 30             | -10            |
| [12k, 12k].1 | 6    | -6.025         | 30             | -10            |
| [12k, 12k].2 | 12   | -6.025         | 30             | -10            |
| [12k, 12k].3 | 12   | -6.027         | 30             | -10            |
| [12k, 12k].4 | 12   | -6.025         | 30             | -10            |
| [12k, 12k].5 | 6    | -6.023         | 30             | -10            |
| [12k, 12k].6 | 6    | -6.017         | 30             | -10            |
| [12k, 12k].7 | 12   | -6.014         | 30             | -10            |
of different configurations with temperature. We note that due to low multiplicity of the configuration $[2a,2a]$, its formation probability falls rapidly as temperature increases. On the other hand, the formation probability of the configuration $[2a,12k]$ (sum of the formation probabilities for all $[2a,12k]$ configurations) increases steeply and reaches a maximum value at 50 K and then falls with temperature. Fig. 5 shows that the formation probability of the $[2a,12k]$ configuration becomes larger that that of $[2a,2a]$ beyond $T \sim 10$ K, which is a much lower transition temperature than in the $x = 0.5$ case.

We can calculate the occupation probability of Al at nonzero temperatures for a given site by adding all formation probabilities of the configurations where at least one Al$^{3+}$ ion is substituted in that site. At the annealing temperature of 1000 K, the occupation probability of Al for 12k site is 79.8% for $x = 0.5$ as given in Table IV. The same probability is increased to 97.7% for $x = 1.0$ as calculated by adding the $P_{1000}$’s for all configurations that contain the 12k site. This means that the fraction of Al$^{3+}$ ions occupying the 12k site increases when the fraction of Al is increased from $x = 0.5$ to $x = 1.0$. This conclusion is in agreement with the previously reported measurements [11,16,35].

In Table III we compare the contribution of different sublattices to the total magnetic moment in Al-substituted SFO. To see the effect of Al$^{3+}$ ions in different substitution sites, we split the entries of sublattices containing these ions (2a and 12k). As expected, Al$^{3+}$ ions carry negligible magnetic moment regardless of their substitution sites. Consequently, when they replace Fe$^{3+}$ ions in the minority spin sites ($4f_1$ and $4f_2$), they eliminate a negative contribution and hence increase the total magnetic moment. On the other hand, when they replace Fe$^{3+}$ ions in the majority spin sites (12k, 2a, and 2b), they eliminate a positive contribution and hence reduce the total magnetic moment. For the $x = 0.5$ case, the most probable sites are 12k and 2a (majority sites) and the net magnetic moment of the unit cell is reduced by 5 $\mu_B$. For the configuration $[2a,12k]$, 1 of the $x = 1.0$ case, two Al atoms are substituted in the 2a and 12k sites, there is a reduction of 10 $\mu_B$ in the total magnetic moment per unit cell.

Magnetic Anisotropy determines the capacity of a magnet to withstand external magnetic and electric fields. This property is of considerable practical interest, because anisotropy is exploited in the design of the most magnetic materials of commercial importance. The magnetocrystalline anisotropy energy (MAE) is one of the main factors that determine the total magnetic anisotropy of the material. To investigate the effect of Al substitution on the magnetic anisotropy of SFO, we computed the MAE and the magnetic anisotropy constant of SrFe$_{12-x}$Al$_x$O$_{19}$ for $x = 0, 0.5$ and 1. The MAE, in the present case, is defined as the difference between the two total energies where electron spins are aligned along two different directions [36].

$$E_{\text{MAE}} = E_{(100)} - E_{(001)}$$

where $E_{(100)}$ is the total energy with spin quantization axis in the magnetically hard plane and $E_{(001)}$ is the total energy with spin quantization axis in the magnetically easy axis. Using the MAE, the uniaxial magnetic anisotropy constant $K_1$ can be computed [37,38].

$$K_1 = \frac{E_{\text{MAE}}}{V \sin^2 \theta}$$

where $V$ is the equilibrium volume of the unit cell and $\theta$ is the angle between the two spin quantization axis orientations (90° in the present case). The anisotropy field $H_a$ can be expressed as [39]

$$H_a = \frac{2K_1}{M_s}$$

where $K_1$ is a magnetocrystalline anisotropy constant and $M_s$ is saturation magnetization.

The results for the MAE, the magnetocrystalline anisotropy constant $K_1$, and anisotropy field $H_a$ for SFO with different Al concentration are presented in Table IV. To compare with experimental results, we also compute the weighted average of $K_1$ and $H_a$ using the formation probability $P_{1000}$ at a typical annealing temperature of 1000 K [11]. We note that SFO considered in the present work loses most of its magnetic properties at typical annealing temperatures (1000 K or higher) that are near or above its Curie temperature. The magnetic properties listed in Table IV refer to their ground state properties at the temperature $T = 0$. We use the formation probability at 1000 K to compute the weighted averages as the crystalline configurations of SFO will be...
TABLE III. Contribution of atoms in each sublattice to the total magnetic moment of Al-substituted SFO structures [12k], [2a], and [2a, 12k]. Compared with pure SFO. All magnetic moments are in μ₀. ∆m is measured relative to the values for the pure SFO. Note that the total magnetic moment of the unit cell (m_{tot}) is slightly different from the sum of local magnetic moments due to the contribution from the interstitial region.

| site | SFO | [12k] | [2a] | [2a, 12k].1 |
|------|-----|-------|------|-------------|
|      | atoms | m     | m     | m          |
| 2d   | 2 Sr | -0.006| -0.006| -0.006     |
| 2a   | 1 Fe | 4.156 | 4.155 | -0.001     |
|      | 1 Fe | 4.156 | 4.156 | 0.00       |
| 2b   | 2 Fe | 8.098 | 8.086 | -0.012     |
| 4f₁  | 4 Fe | -16.152| -16.189| -0.037    |
| 4f₂  | 4 Fe | -16.384| -16.420| -0.036    |
| 12k  | 1 Fe | 4.172 | Al    | 0.000      |
|      |      |       |       | -4.172     |
| 4e   | 4 O  | 1.416 | 1.304 | -0.112     |
| 4f   | 4 O  | 0.360 | 0.281 | -0.079     |
| 6h   | 6 O  | 0.124 | 0.115 | 0.009      |
| 12k  | 12 O | 1.016 | 0.877 | -0.129     |
| 12k  | 12 O | 2.140 | 1.895 | -0.245     |
| ∑ m  |      | 38.980| 34.114| -4.837     |
| m_{tot}| 40   | 35    | -5    | 35         |

TABLE IV. The saturation magnetization (M_s), magnetocrystalline anisotropy energy (MAE), magnetocrystalline anisotropy constant (K₁) and anisotropy field (H_a) for SFO and SFAG. x is the Al fraction in SrFe_{12-x}Al_xO_{19} and V is the volume of the unit cell in Å³. P_{1000} is the formation probability at 1000 K. The averaged quantities are weighted by P_{1000}. M_s is in emu/g, MAE in meV, H_a in kOe, and K₁ in kJ·m⁻³. 

| x    | Config   | M_s | MAE | V       | K₁  | H_a | P_{1000} | ⟨M_s⟩ | ⟨K₁⟩ | ⟨H_a⟩ |
|------|----------|-----|-----|---------|-----|-----|---------|-------|------|-------|
| 0.0  | [2a]     | 96.41 | 0.95 | 703.29   | 216 | 9.38 | 119.19  | 3.75  | 1.00 | 189.19 |
|      | [12k]    | 96.41 | 0.80 | 703.19   | 182 | 7.90 | 0.79    |       |      |       |
| 0.5  | [2a]     | 96.41 | 0.67 | 702.82   | 152 | 6.62 | 0.003   | 96.49 | 189  | 8.18  |
|      | [4f₁]    | 123.96| 0.86 | 704.22   | 196 | 6.61 | 0.001   |       |      |       |
|      | [4f₂]    | 123.96| 0.83 | 702.58   | 189 | 6.38 | 0.001   |       |      |       |
| 1.0  | [2a]     | 82.64 | 0.99 | 698.94   | 227 | 11.41| 0.019   |       |      |       |
|      | [12k]    | 82.64 | 0.88 | 690.08   | 202 | 10.13| 0.379   |       |      |       |
|      | [12k, 4f₂] | 82.64 | 0.75 | 698.66   | 172 | 8.64 | 0.585   |       |      |       |
|      | [12k, 4f₁] | 110.19| 0.78 | 690.64   | 181 | 6.74 | 0.007   |       |      |       |
|      | [12k, 2b] | 110.19| 0.80 | 700.29   | 183 | 6.92 | 0.004   |       |      |       |
|      | [4f₂]    | 137.74| 0.80 | 697.96   | 184 | 5.53 | 0.000   |       |      |       |
|      | [4f₂]    | 137.74| 0.83 | 699.62   | 191 | 5.74 | 0.000   | 83.03 | 184  | 9.23  |
|      | [4f₁]    | 137.74| 0.86 | 701.38   | 196 | 5.95 | 0.000   |       |      |       |
|      | [4f₁]    | 110.19| 0.65 | 699.95   | 149 | 5.62 | 0.000   |       |      |       |
|      | [4f₁]    | 110.19| 0.91 | 700.11   | 208 | 7.87 | 0.001   |       |      |       |
|      | [2b, 2b] | 82.64 | 0.45 | 698.86   | 103 | 5.19 | 0.000   |       |      |       |
|      | [2b, 2a] | 82.64 | 0.74 | 698.82   | 170 | 8.53 | 0.001   |       |      |       |

distributed according to this value during the annealing process.

Table IV shows that M_s decreases as the concentration of Al x is increased from 0 to 0.5 to 1.0, consistent with the previous experimental results [11, 20, 30, 31]. Our calculation also shows that K₁ decreases as the concentration of Al x is increased from 0 to 0.5 to 1.0. At a low temperature Al atoms prefer to occupy the 2a site, which would have increased K₁ (see K₁ values for [2a] and 2a, 2a in Table IV). However, the formation probability of the configurations involving 12k site (such as [12k], [2a, 12k] and [12k, 12k]) increases significantly as the temperature rises due to the entropy contribution of the free energy. At the annealing temperature Al^{3+} ions are much more likely to occupy the 12k site than the 2a site. This causes the magnetocrystalline anisotropy con-
stant $K_1$ of Al-substituted SFO to be reduced with the increase of Al fraction $x$, consistent with the experimental measurement reported by Albanes [40]. Despite of this, $M_s$ is reduced more significantly than $K_1$ and this causes the anisotropy field $H_a$ in Eq. (4) to increase as the concentration of Al $x$ is increased from 0 to 0.5 to 1.0 as shown in Table IV. This result is consistent with several experimental results [1] [41].

IV. CONCLUSIONS

Using the first-principles total energy calculations based on density functional theory, we obtained the ground state structures and associated formation probabilities at finite temperatures for Al-substituted SFO, SrFe$_{12-x}$Al$_x$O$_{19}$ with $x = 0.5$ and $1.0$. The structures derived from our calculations show that the total magnetic moment of the SFO unit cell is reduced as the fraction of Al atoms increases. This reduction of magnetization is explained by the fact that the non-magnetic Al atoms prefer to replace Fe$^{3+}$ ions at two of the majority spin sites, $2a$ and $12k$, eliminating their positive contribution to the total magnetization. Our model also explains the increase of the observed anisotropy field when the fraction of Al in SFO is increased. At the annealing temperature Al$^{3+}$ ions are much more likely to occupy the $12k$ site than the $2a$ site. Although this causes the magnetocrystalline anisotropy to decrease slightly, the reduction in the saturation magnetization is larger and their combined effect causes the magnetic anisotropy field of Al-substituted SFO to be reduced with increase of Al fraction $x$. Our results are consistent with the available experimental measurement on Al-substituted SFO.

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