Co site preference and site-selective substitution in La–Co co-substituted magnetoplumbite-type strontium ferrites probed by $^{59}$Co nuclear magnetic resonance

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Abstract

In the La–Co co-substituted magnetoplumbite-type strontium (Sr–La–Co) ferrite, the base materials of the high-performance hard ferrite magnet, Co tends to occupy more than two crystallographically inequivalent sites. To reveal the Co site preference and the function of each site, $^{59}$Co nuclear magnetic resonance (NMR) spectrum was measured for the Sr–La–Co ferrites with various Co compositions. The intimate correlation between the anisotropy field and the relative intensity of the strongest NMR line clearly indicates that Co occupying the tetrahedrally coordinated 4$f_1$ site is only responsible for the enhancement in the uniaxial anisotropy. In the samples with the Co concentrations much larger than commercial magnets, most Co selectively occupies the 4$f_1$ site, indicating possible tuning of the magnetic performance with limited Co content in the future development. The close correlation between orbital moments and local strain is also demonstrated.

1. Introduction

The economical and chemically stable ferrite magnet is one of industrially important permanent magnets along with rare-earth magnets [1]. The development of high-performance ferrite magnets leads to a large social impact. A recent milestone in this field is the improvement in magnetic performance by the substitution of a small amount of Co for Fe [2]. A typical example is the Sr–La–Co system, in which Fe$^{3+}$ in the Sr magnetoplumbite-type (M-type) ferrite, SrFe$_{12}$O$_{19}$, is substituted by a small amount of Co$^{3+}$ and a part of Sr$^{2+}$ is replaced by La$^{3+}$ to compensate electric charge [2]. Another example is the Ca–La–Co system, in which Sr in the Sr–La–Co system is replaced by Ca [3]. In the M-type ferrite, there are five crystallographically inequivalent Fe sites (2$a$, 2$b$, 4$f_1$, 4$f_2$, and 12$k$ by Wyckoff notations in the space group $P6_3/mmc$). Oxygen coordination is octahedral for 2$a$, 4$f_2$, and 12$k$, tetrahedral for 4$f_1$, and bipyramidal for 2$b$. It is ferrimagnetic with majority-spin at 2$a$, 2$b$, and 12$k$ sites, and minority spin at 4$f_1$ and 4$f_2$ sites. The improvement of the magnetic performance by the Co substitution is mainly ascribed to the increase in the coercivity, namely the enhancement in the uniaxial anisotropy associated with the unquenched orbital magnetic moment of Co$^{3+}$ occupying at particular Fe sites. In both Sr–La–Co and Ca–La–Co systems, Co tends to occupy more than two Fe sites [4–7]. It is likely, however, that Co at particular sites only contributes to the uniaxial anisotropy, while the other Co is useless or even harmful in enhancing magnetic performance. Furthermore, since Co occupation at the majority-spin sites reduces the net magnetization, the Co occupation at the minority-spin sites is preferable in the viewpoint of the saturation magnetization. In order to improve magnetic performance with limited Co content, site-selective Co substitution is highly required; commercially it is important to reduce the usage of Co because of its unstable price and supply. For the Sr–La–Co system, although it was widely believed that Co mainly occupies the octahedrally coordinated 4$f_2$ site [8], it is now gradually accepted that Co mainly occupies the tetrahedrally coordinated 4$f_1$ and partly octahedrally coordinated 2$a$ and/or 12$k$ sites [5, 6, 9, 10]. Furthermore, it has
been revealed that, in the samples synthesized under ambient atmosphere, La$^{3+}$ content, $x$, and Co$^{2+}$ content, $y$, are not necessarily identical but in general $x > y$, and their difference is compensated by the reduction of Fe$^{3+}$ to Fe$^{2+}$ [4, 11–13]. In order to get information on Co occupation sites, we have previously reported the result of $^{59}$Co nuclear magnetic resonance (NMR) experiment for the Sr–La–Co sample synthesized under ambient atmosphere [7]. As principal components, three kinds of $^{59}$Co-NMR lines, S1, S2, and S3, were observed at ~90, 310, and 390MHz, respectively. However, the origin of the anomalously small internal field (~9 T) for the strongest S1 line is yet to be explained. Namely, there are two possibilities; one is the compensation between spin and orbital contributions of high-spin Co$^{2+}$ to the internal field, and the other is the possible presence of octahedrally coordinated Co$^{3+}$ in the low-spin state with $S = 0$. Since we found the Fe valence instability in the Sr–La–Co system, we could not exclude Co valence instability, i.e. the possible coexistence of Co$^{3+}$. Recently, we have shown that a higher oxygen potential during sample synthesis extends the Co solubility limit and increases the anisotropy field almost linearly to the Co concentration [14].

In this study, in order to explain the origin of the S1 line and extract information on the site preference of Co, we performed $^{59}$Co-NMR experiment for the Sr–La–Co ferrites with $x \approx y$ and $x = 0$ prepared under oxygen and ambient atmosphere, respectively, and with much larger $y$ than commercial magnets synthesized under a high oxygen pressure using hot isostatic pressing (HIP). We reveal the function of Co at each site and show a guiding principle to develop high-performance hard ferrite magnet.

### 2. Experimental procedures

Four samples were measured in the present study. One is Sr$_{1.2}$La$_{1.2}$Fe$_{12-y}$Co$_y$O$_{12}$ with $x = 0.32$ and $y = 0.28$, and another with $x = 0$ and $y = 0.07$. The former and latter single crystals were grown by the Na$_2$O flux method under an oxygen gas stream (oxygen partial pressure $p_{O_2} = 1$ atm) and ambient atmosphere ($p_{O_2} = 0.2$ atm), respectively. The compositions of metallic elements, $x$ and $y$, were determined by wavelength-dispersive x-ray spectroscopy (WDX). See [13] for details of the crystal growth and characterization. In synthesizing Sr–La–Co samples under ambient atmosphere, the Co content, $y$, is generally smaller than that of the La concentration, $x$. The first sample was synthesized under an oxygen gas stream to obtain crystals with $x \approx y$. The higher oxygen potential can suppress the appearance of Fe$^{2+}$, which is the origin of the discrepancy between $x$ and $y$. The second is a La-free sample, in which Co is expected to be trivalent because of the lack of degrees of freedom in the electric charge of transition-metal elements. The Co concentration $y = 0.07$ was the maximum limit for the La-free single crystals prepared by the Na$_2$O flux method under ambient atmosphere. The single crystals were crushed to fine powder for the NMR experiment. The others are two Sr–La–Co samples in powder form synthesized using a HIP apparatus. They were synthesized under an oxygen partial pressure of $p_{O_2} = 387$ atm. Their WDX-analyzed compositions are $x = 0.70$, $y = 0.72$ and $x = 0.92$, $y = 0.93$. See [14] for the details of the HIP-synthesized samples. For the samples treated in the present study, lattice parameters at room temperature and the anisotropy field, $H_A$, at 5 K [13, 14] are listed in table 1. The lattice parameters were estimated from powder x-ray diffraction data measured by X’Pert PRO Alpha-1 PANalytical with use of Cu-K$_{α1}$ radiation. $H_A$ was estimated from the area surrounded by easy- and hard-axis magnetization curves, $K_1$, and saturation magnetization, $M_s$, using the relation, $H_A = 2K_1/M_s$. The $^{59}$Co-NMR experiment was done at ICPMS using a nontuned wide-band spectrometer, which ensures good reproducibility of the frequency spectrum. The nuclear quantities for $^{59}$Co are the nuclear spin $I = 7/2$, the gyromagnetic ratio $γ/2\pi = 10.05$ MHz T$^{-1}$, the quadrupole moment $Q = 42.0 \times 10^{-30}$ m$^2$, and a natural abundance of 100%. The $^{59}$Co NMR spectrum was measured at 2 K under zero external field in a frequency range of 30–650 MHz by measuring the spin-echo intensity. The radio–frequency power dependence of the spin-echo intensity was accumulated at each frequency and integrated to obtain the frequency spectrum. In the same process, the frequency-dependent enhancement

| Label | $p_{O_2}$ (atm) | Contents $x$ | Contents $y$ | Lattice parameters at RT $a(\text{Å})$ | $c(\text{Å})$ | $c/a$ | $H_A$ at 5 K (T) | References |
|-------|----------------|--------------|--------------|---------------------------------|-------------|------|----------------|------------|
| A15   | 0.2            | 0.29, 0.15   |             | 5.8829, 23.0148, 3.9122         | 2.157       |      |                | [13]       |
| O28   | 1.0            | 0.32, 0.28   |             | 5.8839, 23.0050, 3.9098         | 2.540       |      |                |            |
| H70   | 387            | 0.70, 0.72   |             | 5.8835, 22.9410, 3.8992         | 3.425       |      |                | [14]       |
| H90   | 387            | 0.92, 0.93   |             | 5.8837, 22.9105, 3.8939         | 4.242       |      |                | [14]       |
| N07   | 0.2            | 0, 0.07      |             | 5.8838, 23.0400, 3.9158         | 1.713       |      |                |            |
factor was determined and used to correct the NMR intensities. These intensities were then employed to estimate the population ratio of the Co atoms which sense the corresponding local fields [15].

3. Results and discussion

3.1. Site assignments of $^{59}$Co-NMR signals

Figure 1 shows $^{59}$Co-NMR spectra for the Sr–La–Co samples synthesized under the oxygen gas stream ($x = 0.32, y = 0.28$) and by HIP ($x = 0.70, y = 0.72$ and $x = 0.92, y = 0.93$), together with that synthesized under ambient atmosphere ($x = 0.29, y = 0.15$) reported previously [7]. These samples are labeled as A15, O28, H72, and H93 in order of Co concentration, $y$. Figure 1 shows 59Co-NMR spectra for samples A15, O28, H70, and H90 measured at zero applied field and at 2 K. Intensities were normalized to directly represent the amount of Co in such a way that the total integrated intensity of each material is in proportion to the Co concentration, $y$. The inset shows a magnified view of the S2 and S3 part.

Figure 1. $^{59}$Co-NMR spectra for samples A15, O28, H70, and H90 measured at zero applied field and at 2 K. Intensities were normalized to directly represent the amount of Co in such a way that the total integrated intensity of each material is in proportion to the Co concentration, $y$. The inset shows a magnified view of the S2 and S3 part.
has already been done by Morel et al [8] for the data reported by Pieper et al [16], although their Co site assignment is essentially different from ours, as discussed below. The other possibility is the presence of low-spin (i.e. nonmagnetic) Co$^{2+}$ at some of the octahedrally coordinated sites if Co valence were unstable like that of Fe. We do not consider the presence of low-spin Co$^{2+}$, which is generally unrealistic. To conclude this problem, we measured O28 with $x \approx y \approx 0.3$, together with N07 for $x = 0$. Since the charge compensation between La$^{3+}$ and Co$^{2+}$ roughly holds in O28 owing to the suppression of Fe$^{2+}$, we expect that O28 includes Co$^{2+}$ only. In contrast, we expect that N07 includes Co$^{3+}$ only. From the fact that S1 is still strongest in O28, we can assign S1 to Co$^{2+}$. The fact that none of S1, S2, and S3 was observed in N07 strongly suggests that all of S1, S2, and S3 come from Co$^{3+}$. In fact, for N07, another sharp$^{59}$Co signal, which can be assigned to low-spin Co$^{3+}$, has been observed at $\sim$50 MHz in a completely different radio-frequency pulse condition [9]. This low-spin Co$^{3+}$ signal has not been observed for A15 and O28. Thus, all S1, S2, and S3 are reasonably assigned to high-spin Co$^{3+}$, and their different resonance frequencies are ascribed to the difference in $m_{\text{int}}$. The diveral high-spin state of Co is also supported by Co K$_{	ext{J}}$ x-ray emission spectroscopy [10]. Recently, Kobayashi et al [5] claimed that Co occupies 4$f_{1}$, 2$a$, and 12$k$ sites from the results of x-ray absorption spectroscopy (XAS) combined with neutron diffraction Rietveld refinement analysis. In addition, they claimed from the results of hard x-ray magnetic circular dichroism (MCD) experiment that Co occupies the tetrahedrally coordinated, namely 4$f_{1}$, site. Our independent XAS and MCD experiments corroborated by first-principle calculations confirmed their conclusion (unpublished). Analyses of$^{57}$Fe NMR and Mössbauer spectra also support the conclusion [9, 10]. Thus, we assign the strongest S1 line to 4$f_{1}$-Co and S2/S3 to 2$a/12$k-Co. So far, we have not succeeded in distinctively assigning 2$a$- and 12$k$-Co.

3.2. Co site preference and its correlation with anisotropy

As seen in figure 1 and table 2, for the samples synthesized under high oxygen partial pressure, the relative intensity of S1 is markedly enhanced compared with those of S2 and S3. The result indicates that, in the HIP-synthesized samples, not only that Co preferentially occupies the 4$f_{1}$ site, but also that the Co occupation at the site corresponding to S2 tends to be suppressed, contrary to no appreciable variation in S3. Thus, the higher oxygen potential not only expands the Co solubility limit, but also enhances the Co site selectivity. This result demonstrates that, by controlling appropriate parameters, the magnetic performance of the ferrite magnet can be tuned with limited Co content. As listed in table 1, the anisotropy field (at 5 K), $H_{\text{an}}$, increases almost linearly to the amount of 4$f_{1}$-Co, demonstrating intimate correlation between the uniaxial anisotropy and, particularly, tetrahedrally coordinated 4$f_{1}$-Co.

One of the important characteristics of NMR for ferromagnetic (or ferrimagnetic) materials is the effect of signal enhancement. The effective oscillating field at the nuclear site, $H_{\text{eff}}$, is amplified by the oscillation of the internal field, $H_{\text{int}}$ produced by electronic moments following the operating radio-frequency field, $H_{r}$. Therefore, the enhancement factor $\eta = H_{\text{eff}} / H_{r}$ gives the information on magnetic stiffness of the corresponding electronic moment, namely local anisotropy at the corresponding site. The local stiffness is usually represented by the restoring field, $H_{r}$, which is the necessary field to recover electronic moments to the equilibrium and defined as $\eta = H_{\text{int}} / H_{r}$. $H_{r}$ is given from optimum $H_{r_{1}}$ by $H_{r_{1}} = \beta H_{J_{1}}$, where $\beta$ is a constant depending only on nuclide and experimental setup [15]. Figure 2 shows $H_{r}$ which gives optimal intensity of S1, namely for 4$f_{1}$-Co, plotted as a function of Co concentration, $y$. $H_{r}$ for 4$f_{1}$-Co increases appreciably and almost linearly to $y$. This behavior is in good accordance with the trend of $H_{K_{z}}$ (see the broken line in figure 2) but in good contrast to $H_{r}$ for S2 and S3 (inset of figure 2), which rather decrease with $y$. This result clearly demonstrates that 4$f_{1}$-Co correlates with the anisotropy enhancement, while 2$a/12$k-Co acts negatively on the uniaxial anisotropy; 2$a/12$k-Co may prefer to planar or cone anisotropy.

| Sample | Contents | Resonance frequency (MHz) (Internal field (T)) | Co relative occupation ratio (Co concentration) |
|--------|----------|-----------------------------------------------|-----------------------------------------------|
|        | $x$      | $y$  | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 |
| A15    | 0.29     | 0.15 | 86 | 307| 386| 529| 0.745 | 0.155 | 0.100 | <0.002 |
|        |          |      | (8.6) | (30.5) | (38.4) | (52.6) | (0.112) | (0.023) | (0.015) | <0.0003 |
| O28    | 0.32     | 0.28 | 84 | 308| 389| 529| 0.830 | 0.087 | 0.083 | <0.002 |
|        |          |      | (8.4) | (30.6) | (38.7) | (52.6) | (0.232) | (0.024) | (0.023) | <0.0006 |
| H70    | 0.70     | 0.72 | 81 | 325| 399| — | 0.963 | 0.012 | 0.025 | — |
|        |          |      | (8.1) | (32.3) | (39.7) | — | (0.693) | (0.009) | (0.018) | — |
| H90    | 0.92     | 0.93 | 79 | 329| 401| — | 0.973 | 0.005 | 0.022 | — |
|        |          |      | (7.9) | (32.7) | (39.9) | — | (0.905) | (0.004) | (0.021) | — |
In the octahedral case for state with an unquenched orbital moment the coordination polyhedra are shrunk along local strain at the respective site, as generally expected. In the Sr dominated by the lattice deformation, suggesting strongly that the orbital contribution principally depends on variation for $S_2$ and $S_3$ indicates opposite tendencies for $2$ relatively low site symmetry lower than the $(dz^2-r^2)$ $\text{g doublet}$ and the $2g$ triplet in cubic crystal.

The low resonance frequency for $S_1$ is reasonable provided that the orbital moment at $4\text{-Co}$ orbital is smaller than those at $2a/12k$-$\text{Co}$. Assuming a constant spin moment regardless of the occupation site and the magnitude of the orbital moment, and applying the coupling constants $A_{\text{spin}} = -12 T / \mu_B$ and $A_{\text{orb}} = 65 T / \mu_B$, relatively large orbital moments of $0.4 \mu_B$ and $1.0 - 1.2 \mu_B$ are estimated for $4f_1$- and $2a/12k$-$\text{Co}$, respectively. We assumed that signs of the observed internal fields are all positive for $S_1$, $S_2$, and $S_3$. The applied field dependence of the resonance frequency for $S_1$ showed that the sign of the net internal field is positive for $S_1$ [9]. Positive internal fields can be reasonably assumed also for $S_2$ and $S_3$ because larger orbital moments are expected for octahedrally coordinated $2a/12k$-$\text{Co}$.

### 3.3. Correlation between orbital moments and local strain

As seen in figure 1, with increasing Co concentration, $y$, $S_1$ slightly shifts to lower frequencies, whereas $S_2$ and $S_3$ shift to higher frequencies. The central frequencies of $S_1$, $S_2$, and $S_3$ are plotted in figure 3 against $y$, where they all show good linearity with $y$. As mentioned above, the net internal fields are determined from the sum of spin and orbital contributions. Applying the same assumptions above (positive internal fields for all Co and the $y$- and site-independent spin component), the variation is ascribed to the change in the orbital component. The negative $y$ dependence of $S_1$ implies that the $4f_1$-$\text{Co}$ orbital field decreases with increasing $y$, whereas the positive variation for $S_2$ and $S_3$ indicates opposite tendencies for $2a/12k$-$\text{Co}$.

The inset of figure 3 shows the $c/a$ ratio plotted against $y$, where $a$ and $c$ are lattice parameters. Despite that the lattice parameter $a$ itself does not necessarily vary systematically against $y$ (see table 1), $c/a$ shows an excellent linearity to $y$ just like the resonance frequencies in figure 3. This indicates that the frequency shifts in figure 3 is dominated by the lattice deformation, suggesting strongly that the orbital contribution principally depends on local strain at the respective site, as generally expected. In the Sr-La-\text{Co} system, the decrease in $c/a$ implies that the coordination polyhedra are shrunk along $c$. At the octahedrally coordinated $2a$ and $12k$ sites, we expect that the $dz^2$ singlet and the $(dx^2-r^2 + dy^2)$ doublet are more separated, resulting in a higher population in the doublet.
degenerate ground state with the unquenched orbital moment. In contrast, at the tetrahedrally coordinated 4\textit{f}_1 site, the decrease in \(c/a\) makes the split between the \(d_{z^2}\) singlet and the \((d_{xy}^2 + d_{yz})\) doublet narrower, reducing excitations to the \(t_{2g}\)-derived orbital, consequently leading to smaller orbital moment. These tendencies are in good agreement with our experimental observations, and, at the same time, support strongly our site assignments in section 3.1. The reduction in the orbital contribution at 4\textit{f}_1-Co is rather unfavorable for enhancing the uniaxial anisotropy, but seems to be overwhelmed by the appreciable increase in the Co occupation at the 4\textit{f}_1 site. It is likely that 2\textit{a}/12\textit{k}-Co atoms do not contribute to the anisotropy enhancement, even if they have larger orbital moments, possibly because they prefer to planar or cone anisotropy. The Co site selectivity may also be related to the local strain because the Ca–La–Co system with smaller \(c/a\) ratios tends to show larger anisotropy at smaller Co contents [3].

4. Conclusions

We have performed \(^{59}\text{Co}-\text{NMR}\) experiments for Sr–La–Co ferrites with different Co compositions prepared under different oxygen potentials. Assigning the S1 resonance at the lowest frequency to high-spin Co\(^{2+}\) at the tetrahedrally coordinated 4\textit{f}_1 site, and S2 and S3 at higher frequencies to high-spin Co\(^{2+}\) at the octahedrally coordinated 2\textit{a} and 12\textit{k} sites, intimate correlation between tetrahedrally coordinated 4\textit{f}_1-Co and the anisotropy field is demonstrated. The application of high oxygen pressure leads to site-selective Co occupation at the tetrahedrally coordinated 4\textit{f}_1 site. This result indicates that, if Co can be concentrated in the 4\textit{f}_1 site by controlling appropriate parameters, the magnetic performance of the hard ferrite magnet can be tuned more efficiently with limited Co content in the future development. Our result also suggests strongly that the orbital contribution to the magnetic moment, which is closely related to the enhancement in the magnetic anisotropy, is dominated by the local strain at the respective Co site.

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