Determination of Occupation Sites of Co Doped in a (Sr, La)-M type Ferrite by Electron Channeling Microanalysis

K. Hattori[1], S. Muto[1], K. Tatsumi[1], Y. Kobayashi[2], T. Kawada[2]

[1]Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
[2]Hitachi metal, Ltd., Osaka 618-0013, Japan

It has been shown that the magneto-crystalline anisotropy of hexagonal Sr-M type ferrites, as promising hard magnet materials, can be improved by substituting La and Co for Sr and Fe, respectively ($Sr_{0.8}La_{0.2}Fe_{11.4}Co_{0.2}O_{19}$). Two contradictory results were reported on which Fe site, $4f_1$ [1] or $4f_2$ [2] in the Wyckoff's notation of the M-type structure, the key element, Co mainly occupied.

In the present study, in order to understand the guiding principle for realizing better magneto-crystalline anisotropy, we attempted to determine by an electron channeling microanalysis technique for which Fe sites Co is actually substituted, based on the seven structural candidates obtained by neutron diffraction/Rietveld analysis [1]. In Table 1 the occupancies of Co replacing the Fe sites in each model are listed.

High angular resolution electron channeling X-ray spectroscopy (HARECXS) applied [3], using JEM-ARM200F equipped with EDX, where the incident beam direction was digitally controlled. The incident beam directions were continuously tilted around the $[\bar{1}10]$ and $[\bar{7}72]$ zone axes, with 002 and $\bar{1}\bar{1}0$ systematic row excited, respectively. Cross sections for X-ray emission were calculated as functions of the incident beam direction, using the ICSC code [4], assuming the atomic Co occupancies in the models, to compare the experimental results. We confirmed in advance that the experimental and calculated peak intensity ratios of the primary elements, $I_{\text{Sr-L}}/I_{\text{Fe-K}}$ are in good agreement within the experimental inaccuracies.

Figures 1 and 2 show the experimental peak intensity ratio, $I_{\text{Co-K}}/I_{\text{Fe-K}}$ (dots) as a function of the incident beam direction respectively for the $[\bar{1}10]$ and $[\bar{7}72]$ zones compared with the calculated ones (solid lines) based on the models. The error bars were derived simply from the uncertainty of the peak area measurements. The experimental data points significantly fluctuate partly because of the very low count rate of Co-K peak. To quantitatively judge which model best fits the experimental data, we defined the following measure:

$$var = \sum_{i=1}^{N}(y_{i,\text{exp.}} - y_{i,\text{calc.}})^2/N, \qquad (1)$$

where N is the number of measured points, and $y_{i,\text{exp.}}$ and $y_{i,\text{calc.}}$ are the experimental and calculated $I_{\text{Co-K}}/I_{\text{Fe-K}}$, respectively. The values are shown in Table 2 for the models. It is consequently safely concluded that model 6 and 7 are most consistent with the experiment and the key occupation site of Co is $4f_1$, which is also consistent with the XAFS analysis [1].

References

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Table 1 Seven candidate models derived from the neutron diffraction and its Rietveld analysis, showing the occupation sites and occupancies of Co. The symbols, 2a, 2b, $4f_1$, $4f_2$ and 12k are the Wyckoff's notation of the Fe sites

Model#	2a	2b	$4f_1$	$4f_2$	12k
1	-	-	0.100	-	-
2	-	-	-	-	0.033
3	0.069	-	0.066	-	-
4	0.063	-	-	-	0.023
5	-	-	0.088	0.012	-
6	-	-	0.047	-	0.018
7	0.043	-	0.039	-	0.013

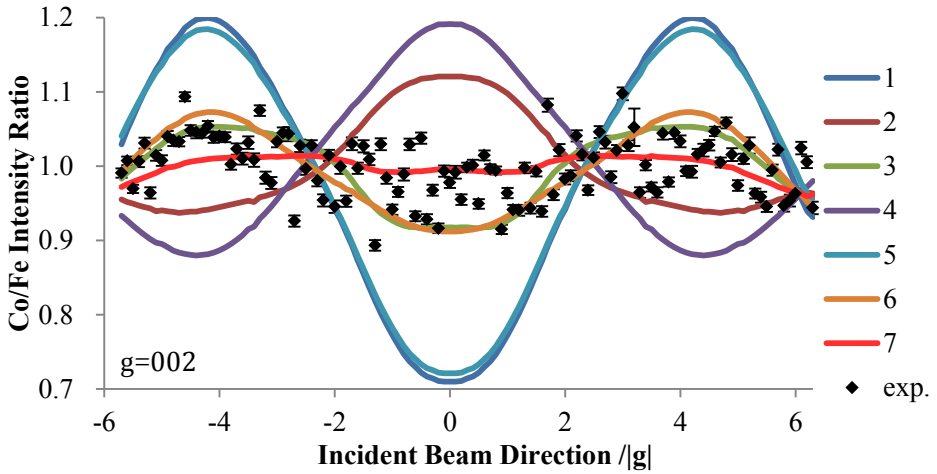

Figure 1 The measured $I_{Co\text{-}K}/I_{Fe\text{-}K}$ (dots) and model simulations (lines) around the $[\bar{1}10]$ zone axis.

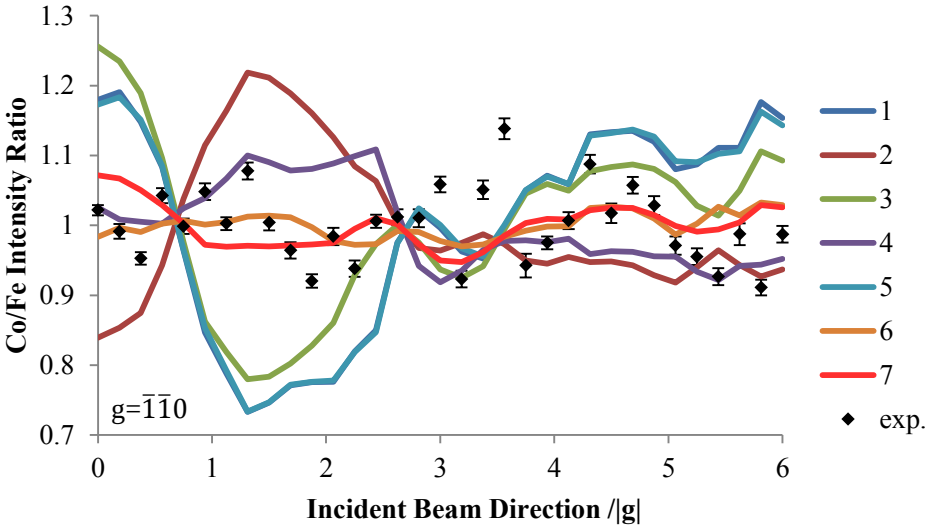

Figure 2 The same as Figure 1 but around the $[\bar{7}72]$ zone axis.

Table 2 The calculated *var* in Eq.(1) in units of 10^{-3} for each model for the two experiments above.

Zone axis	1	2	3	4	5	6	7
$[\bar{1}10]$	22.8	7.95	2.09	16.6	20.5	2.36	1.39
$[\bar{7}72]$	23.7	12.8	17.6	6.13	23.1	3.01	3.69