Order-disorder and magnetic exchange interactions in substituted strontium hexaferrite $SrA_xFe_{12-x}O_{19}(A=Ga, In)$

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The unusual magnetic behavior of the $12k$ site in $SrGa_xFe_{12-x}O_{19}$ ($0.3 \leqslant x \leqslant 6.0$) and $SrIn_xFe_{12-x}O_{19}$ ($0.3 \leqslant x \leqslant 1.4$) has been investigated by means of ^{57}Fe Mössbauer spectroscopy at 298 K. The bifurcation of the $12k$ Mössbauer subspectrum into $12k_1$ and $12k_2$ components of widely differing intensities has been confirmed for both Ga^{3+} and In^{3+}. The bifurcation is apparent at x values as low as 0.3, and the less intense $12k_2$ pattern corresponds to an abrupt drop in the hyperfine magnetic field H_{eff}, of 50 and 75 kOe for Ga^{3+} and In^{3+}, respectively. H_{eff} for the more intense $12k_1$ pattern is virtually unchanged from that of pure $SrFe_{12}O_{19}$ for x values as high as 1.0. Room-temperature Mössbauer spectra confirm that the Ga^{3+} and In^{3+} ions preferentially occupy the $4f_2$ octahedral site. There are indications, however, that the dopants also enter the $2b$ trigonal-bipyramidal site. The change in H_{eff} at the $12k$ sites indicates that complex and competing exchange interactions are present, and that the splitting of the $12k$ magnetic hyperfine spectrum is not due simply to random disruptions of the exchange interactions. The intensities of the $12k_1$ and $12k_2$ subspectra have been used to model the exchange interactions at the $12k$ site.

I. INTRODUCTION

The magnetoplumbite structure, $MFe_{12}O_{19}$ (M=Sr, Ba, Pb), consists of alternating hexagonal ($R=MFe_6O_{11}^{2-}$) and spinel subunits ($S=Fe_6O_8^{2+}$) stacked along the hexagonal c axis. Within the R block are the trigonal-bipyramidal $2b$ and octahedral $4f_2$ Fe^{3+} sites, while the S layer contains the octahedral $2a$ and tetrahedral $4f_1$ Fe^{3+} ions; the $12k$ octahedral Fe^{3+} ions exist at the R-S interface.[1]

In addition to the $2b$ Fe^{3+} site, the octahedral $12k$ site of the M-type hexaferrites exhibits very unusual crystal chemical and magnetic properties. It is clear that an understanding of the high magnetocrystalline anisotropy and of the rapid decrease in the bulk magnetization of the magnetoplumbite hexaferrites depend to a great extent on an understanding of the structure/property relationships for these two sites.

In previous investigations, it was reported that $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ substituted with Sc^{3+}, Ga^{3+}, and In^{3+} exhibited Mössbauer spectra with the $12k$ subpattern split into two components.[2,3] However, there is still some question as to how low a dopant level is required to produce the $12k$ bifurcation. In addition, further analysis of this phenomenon could give valuable insights into the magnetic exchange in-

teractions of the octahedral $12k$ Fe^{3+}. We present the results of such an investigation in this article.

II. EXPERIMENT

Polycrystalline samples of $SrGa_xFe_{12-x}O_{19}$ ($x=0.3$, 0.5, 0.8, 1.0, and 6.0) and $SrIn_xFe_{12-x}O_{19}$ ($x=0.3$, 0.4, 0.8, and 1.4) were prepared from $SrCO_3$, Fe_2O_3, Ga_2O_3, and In_2O_3, using solid-state syntheses similar to those used in earlier reports.[2,3] Electron microprobe analysis (EMPA) and x-ray powder diffractometry were employed to determine the composition, phase purity, and lattice constants of the samples. For each of the substituted hexaferrites, room-temperature ^{57}Fe Mössbauer spectra were collected and analyzed as described in detail in a previous article.[4]

III. RESULTS AND DISCUSSION

The lattice parameters of substituted $SrFe_{12}O_{19}$ are presented in Table I; as evident in Fig. 1, Vegard's law is followed by both solid solution series.[5] As expected, increasing

TABLE I. Lattice constants of substituted $SrFe_{12}O_{19}$.

	x	a (Å)[a]	c (Å)[a]
$SrGa_xFe_{12-x}O_{19}$	0	5.884	23.06
	0.3	5.879	23.05
	0.5	5.880	23.06
	0.8	5.877	23.06
	1.0	5.877	23.06
	6.0	5.831	23.04
$SrIn_xFe_{12-x}O_{19}$	0	5.884	23.06
	0.4	5.893	23.09
	0.8	5.902	23.13
	1.4	5.916	23.18

[a]The error is ± 0.002 and ± 0.02 Å for a and c, respectively.
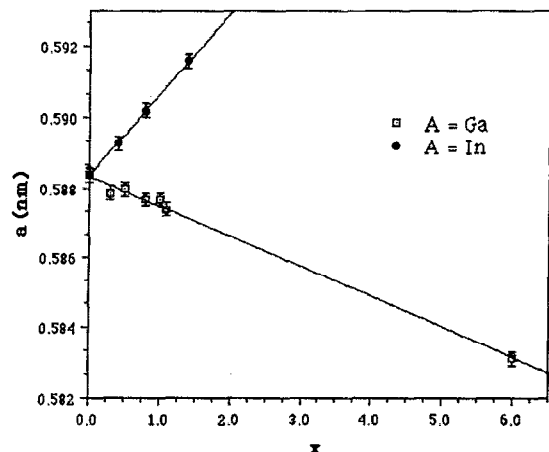

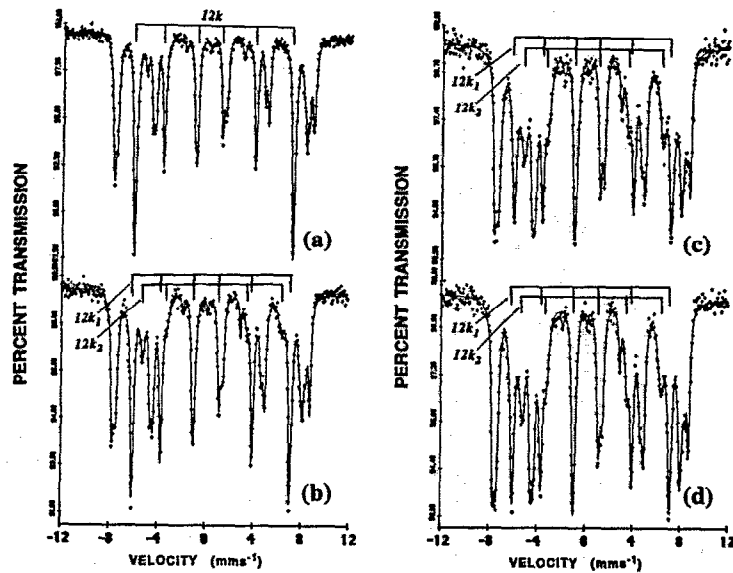FIG. 1. Plot of lattice parameter a vs moles of dopant per formula unit for $SrA_xFe_{12-x}O_{19}$.

FIG. 2. ^{57}Fe Mössbauer spectra of polycrystalline $SrGa_xFe_{12-x}O_{19}$ at 298 K: (a) $x=0$; (b) $x=0.3$; (c) $x=0.5$; (d) $x=1.0$.

substitution of Fe^{3+} by the smaller Ga^{3+} ions results in a gradual decrease in the dimensions of the unit cell, while introduction of the larger In^{3+} ions has the opposite effect.

Selected Mössbauer spectra of $SrGa_xFe_{12-x}O_{19}$ and $SrIn_xFe_{12-x}O_{19}$ at 298 K are shown in Figs. 2 and 3, respectively; the hyperfine interaction parameters are presented in Tables II and III. In the case of both substituted hexaferrites, the bifurcation of the $12k$ subspectrum is visible at a dopant concentration as low as 0.3 mol per formula unit. H_{eff} for $12k_1$ in $SrGa_xFe_{12-x}O_{19}$ is essentially unchanged from that of the unsplit $12k$ pattern in $SrFe_{12}O_{19}$. However, as the In^{3+} ion concentration increases in $SrIn_xFe_{12-x}O_{19}$, H_{eff} for the $12k_1$ does decrease somewhat from that of the $12k$ pattern in $SrFe_{12}O_{19}$.

For the $12k_2$ subspectrum of $SrGa_xFe_{12-x}O_{19}$ and $SrIn_xFe_{12-x}O_{19}$, H_{eff} is roughly constant at, respectively, 50 and 75 kOe lower than that of the $12k$ pattern for $SrFe_{12}O_{19}$. Despite the near constancy of H_{eff} for the $12k_2$ subspectrum, its intensity exhibits remarkable increases as x increases. Indeed, for $x \approx 1.0$ and 0.8 for Ga^{3+} and In^{3+}, respectively, the $12k_1$ and $12k_2$ subspectra have comparable relative intensities. By the time x reaches a value of 6.0 for $SrGa_xFe_{12-x}O_{19}$, the Mössbauer spectrum at 298 K consists only of a pair of partially resolved quadrupole doublets, indicating a significant drop in the Curie temperature T_C.

Analysis of the area ratios of the Mössbauer spectra (Tables II and III) confirms that the dopant ions are entering the octahedral $4f_2$ site. In compensation for the loss of in-
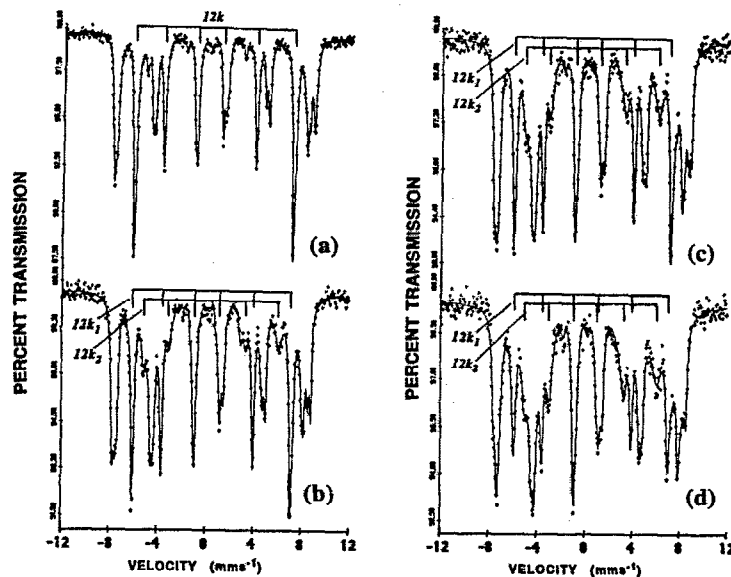

FIG. 3. ^{57}Fe Mössbauer spectra of polycrystalline $SrIn_xFe_{12-x}O_{19}$ at 298 K: (a) $x=0$; (b) $x=0.4$; (c) $x=0.8$; (d) $x=1.4$.

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TABLE II. ^{57}Fe Mössbauer parameters for SrGa$_x$Fe$_{12-x}$O$_{19}$ at 298 K.

x	Fe^{3+} site	H_{eff}[a] (mm s^{-1})	ΔE_Q[a] (mm s^{-1})	δ[a] (mm s^{-1})	Area %
0	2a	503	0.01	0.36	5.9(4)
0.3		499	0.10	0.36	9(1)
0.5		497	0.12	0.35	8(1)
0.8		494	0.14	0.36	9(2)
1.0		495	0.16	0.36	9(1)
0	2b	408	2.26	0.30	6.8(6)
0.3		408	2.16	0.25	5.6(7)
0.5		405	2.20	0.27	5.6(8)
0.8		402	2.21	0.27	6(1)
1.0		399	2.02	0.18	8(2)
0	4f_1	491	0.16	0.26	18(1)
0.3		484	0.17	0.27	22(1)
0.5		482	0.15	0.27	21(1)
0.8		477	0.13	0.27	22(2)
1.0		476	0.11	0.26	25(1)
0	4f_2	518	0.27	0.36	20(1)
0.3		514	0.26	0.37	14(1)
0.5		512	0.26	0.37	16(1)
0.8		509	0.26	0.37	12(1)
1.0		508	0.26	0.36	9.6(5)
0	12k_1	411	0.39	0.35	49(1)
0.3		411	0.39	0.35	41(1)
0.5		411	0.39	0.35	36(1)
0.8		409	0.40	0.35	32(1)
1.0		408	0.39	0.35	28(1)
0	12k_2	...	...	...	...
0.3		358	0.44	0.40	9(1)
0.5		362	0.40	0.36	13(1)
0.8		361	0.41	0.37	19(1)
1.0		359	0.44	0.38	20(1)

[a]Estimated errors in H_{eff}, ΔE_Q, and δ (relative to Fe metal) are ± 1 kOe, ± 0.03 mm s^{-1}, and ± 0.02 mm s^{-1}, respectively.

TABLE III. ^{57}Fe Mössbauer parameters for SrIn$_x$Fe$_{12-x}$O$_{19}$ at 298 K.

x	Fe^{3+} site	H_{eff}[a] (mm s^{-1})	ΔE_Q[a] (mm s^{-1})	δ[a] (mm s^{-1})	Area %
0	2a	503	0.01	0.36	5.9(4)
0.3		492	0.24	0.43	6.9(3)
0.4		492	0.28	0.44	8.8(7)
0.8		492	0.27	0.45	15(2)
1.4		481	0.28	0.44	10(1)
0	2b	408	2.26	0.30	6.8(6)
0.3		390	1.91	0.18	7.4(1)
0.4		388	1.77	0.18	6.4(7)
0.8		392	1.98	0.18	5.7(8)
1.4		388	1.99	0.17	6.0(9)
0	4f_1	491	0.16	0.26	18(1)
0.3		486	0.10	0.26	26(0)
0.4		486	0.07	0.25	28(1)
0.8		483	0.07	0.23	27(1)
1.4		474	0.09	0.23	22(2)
0	4f_2	518	0.27	0.36	20(1)
0.3		514	0.28	0.37	13(0)
0.4		513	0.27	0.37	11(0)
0.8		510	0.28	0.37	7(1)
1.4		503	0.38	0.36	5.4(7)
0	12k_1	411	0.39	0.35	49(1)
0.3		408	0.38	0.36	31(0)
0.4		409	0.38	0.36	32(1)
0.8		407	0.38	0.35	27(1)
1.4		403	0.38	0.36	21(1)
0	12k_2	...	...	...	...
0.3		339	0.46	0.40	16(0)
0.4		338	0.50	0.42	15(1)
0.8		337	0.50	0.39	23(2)
1.4		334	0.52	0.41	30(1)

[a]Estimated errors in H_{eff}, ΔE_Q, and δ (relative to Fe metal) are ± 1 kOe, ± 0.03 mm s^{-1}, and ± 0.02 mm s^{-1}, respectively.

tensity in the 4f_2 pattern, the areas of the octahedral 2a and tetrahedral 4f_1 subspectra increase with the dopant concentration; the area of the combined 12k_1 and 12k_2 subspectra remains essentially constant. There also appears to be a small decrease in the area of the trigonal-bipyramidal 2b pattern, suggesting the occurrence of some substitution in the site. The large uncertainties of the area-percent values in the various subspectra, however, do not allow for a more definitive conclusion in the case of the 2b pattern.

IV. CONCLUSION

This investigation has verified that doping SrFe$_{12}$O$_{19}$ with as little as 0.3 mol per formula unit of Ga^{3+} or In^{3+} ions results in the bifurcation of the 12k octahedral subspectrum. This splitting is due to a change in the magnetic exchange interactions of some of the 12k Fe^{3+} ions as increasing amounts of the diamagnetic dopant enter the 4f_2 site, and possibly the 2b site. The fact that the magnitude of the hyperfine magnetic field of the 12k_1 and 12k_2 patterns remains almost constant with increasing levels of substitution implies that the 12k splitting is not due simply to random changes in the exchange interactions.

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