

^{57}Fe Mössbauer spectroscopic investigation of complex magnetic structures in Ga, Sc, and In substituted M -type hexagonal ferrites

T. M. Clark, B. J. Evans,^{a)} and G. K. Thompson

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

S. Freeman

Hewlett-Packard, Mailstop 1LS-K, Santa Rosa, California 95403

Investigation of preliminary evidence that Ga, Sc, and In influence the bulk and dynamic magnetic properties of hexagonal ferrites by means other than those supported in existing models has been undertaken. In $\text{SrFe}_{12-x}\text{M}_x\text{O}_{19}$ ($\text{M}=\text{Ga}, \text{In}$) and $\text{BaFe}_{12-x}\text{Sc}_x\text{O}_{19}$, the predominant $12k$ sublattice exhibits a remarkable splitting into two distinct subpatterns, $12k_1$ and $12k_2$: At $x=0.3$, hyperfine fields, H_{eff} for $12k_1$ are 411, 408, and 405 kOe, respectively, and for $12k_2$ are 358, 339, and 311 kOe, respectively. The $12k_1$ hyperfine field values are virtually unchanged from that of the pure hexagonal ferrites and are independent of substitution level. Contrastingly, the abruptness of the drop in the $12k_2$ hyperfine field and its dependence on the nature of the substituting cation are remarkable. The relative intensity of the $12k_2$ component correlates with the concentration of nonmagnetic species on the $2b$ and $4f_2$ sites and with the magnetic anisotropy. Scandium seems to have a more profound influence on the magnetic structure and interactions than indium or gallium. Further, at technically significant substitution levels, H_{eff} of the different sublattices exhibit broad and overlapping distributions of values far removed from their distinctiveness in the pure hexaferrites. Thus, the net magnetization of Ga, Sc, and In-doped hexaferrites results from a complex interplay of magnetic dilution on the $2b$ site, enhancement of the magnetization through substitutions on the $4f_2$ site, and a complex influence from the substitution-induced $12k_2$ sublattice.

© 1999 American Institute of Physics. [S0021-8979(99)53708-0]

INTRODUCTION

Models for the substitution of various cations in tailoring the bulk magnetic properties of spinel ferrites are not always transferable to the magnetoplumbite (M type) hexagonal ferrites and while influences on the bulk magnetic properties may indeed approximate those desired, the molecular mechanisms that bring about the change may be entirely different from those on which the substitution scheme is based. This dissonance between the model of crystal and chemical structures for influencing a bulk magnetic property through cation substitution and the experimentally observed crystal/chemical structures appears to be particularly significant in the substitution of Ga, Sc, and In in $\text{BaFe}_{12}\text{O}_{19}$ in attempts to control the anisotropy fields and ferromagnetic resonance linewidths.¹

Gallium, scandium, and indium substitutions in $\text{BaFe}_{12}\text{O}_{19}$ have been found to lead to improvements in the anisotropy fields, ferromagnetic resonance linewidths, and resistivity.¹⁻³ The mechanisms by which these substitutions bring about these effects have been regarded as minor perturbations on the fundamental magnetoplumbite (M type) hexagonal ferrite structure and the related magnetic interactions and are based on single-ion properties. Other investigations have indicated that this is far from the observed situation and that these substitutions, even at relatively low concentration levels, bring about profound changes in the magnetic structures of both $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$ and

that the apparent achievement of the desired properties is quite accidental.^{4,5}

In order to escape the limitations imposed by considering only a single end-member composition, both $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$ have been substituted with Ga, Sc, and In at concentrations that would also allow estimates of the substitution levels at which the onset of the divergence between the model predictions and the observed interactions and structures occurs.

EXPERIMENT

The synthesis of polycrystalline M -type hexagonal ferrites employed in this investigation have been described in detail in earlier reports.^{6,7} A technically relevant Sc-doped Ba hexaferrite was also provided by a commercial source. ^{57}Fe Mössbauer transmission spectra were obtained at 298 K and analyzed as described in an earlier report.^{4,7} The ^{57}Fe Mössbauer spectra of Ga, Sc, and In substituted Ba- and Sr-hexagonal ferrite are presented in Figs. 1 and 2, with ^{57}Fe Mössbauer parameters given in Table I.

RESULTS AND DISCUSSION

The substitution pattern of Ga, Sc, and In for iron in the sublattices of Ba- and Sr-hexaferrites display commonalities. At dopant levels below 1 mole per formula unit, these cations substitute preferentially into the $4f_2$ sublattice. This is illustrated by the data in Table I; while the $4f_2$ subspectrum of $\text{SrFe}_{12}\text{O}_{19}$ has a relative intensity of 20%,⁶ the substitution of gallium or indium for iron results in a sharp

^{a)}Electronic mail: bjmag@umich.edu

TABLE I. ^{57}Fe hyperfine parameters at 298 K for doped hexaferrites. (Estimated standard errors in H_{eff} , ΔE_Q , δ , intensity: ± 1 kOe, ± 0.03 mm s $^{-1}$, ± 0.02 mm s $^{-1}$, and $\pm 2\%$, respectively.)

Composition	Fe $^{3+}$ site	H_{eff} (kOe)	ΔE_Q (mm s $^{-1}$)	δ (mm s $^{-1}$)	Relative intensity ^a (%)
SrFe $_{11.7}\text{Ga}_{0.3}\text{O}_{19}$	2 <i>b</i>	408	1.26	0.25	7
	4 <i>f</i> ₂	514	0.26	0.37	14
	12 <i>k</i> ₁	411	0.39	0.35	41
	12 <i>k</i> ₂	358	0.44	0.40	9
SrFe $_{11.0}\text{Ga}_{1.0}\text{O}_{19}$	2 <i>b</i>	399	2.02	0.18	7.5
	4 <i>f</i> ₂	508	0.26	0.36	9.4
	12 <i>k</i> ₁	409	0.39	0.35	28
	12 <i>k</i> ₂	359	0.44	0.38	20
SrFe $_{11.7}\text{In}_{0.3}\text{O}_{19}$	2 <i>b</i>	390	1.91	0.18	7.5
	4 <i>f</i> ₂	514	0.28	0.37	13
	12 <i>k</i> ₁	408	0.38	0.36	31
	12 <i>k</i> ₂	339	0.46	0.40	16
BaFe $_{11.75}\text{Sc}_{0.25}\text{O}_{19}$	2 <i>b</i>	397	2.28	0.27	4
	4 <i>f</i> ₂	505	0.17	0.43	16
	12 <i>k</i> ₁	409	0.40	0.39	46
	12 <i>k</i> ₂	320	0.40	0.41	5
Technical sample	2 <i>b</i>	392	2.20	0.27	3
1.4% Sc 3000 ppm Mn	2 <i>a</i> +4 <i>f</i> ₂	492	0.18	0.38	23
	12 <i>k</i> ₁	404	0.40	0.37	35
	12 <i>k</i> ₂	320	0.28	0.43	18

^aPercentage of the total area of the overall spectrum.

decrease of the 4*f*₂ relative intensity. A similar decrease is observed when scandium is doped in BaFe $_{12}\text{O}_{19}$, although in this case some scandium also substitutes into the 2*b* sublattice. In no instance does it appear that substituents are entering either the 2*a* or the 4*f*₁ sublattice.

As may be observed in Figs. 1 and 2, a bifurcation of the predominant 12*k* sublattice into two distinct subpatterns, 12*k*₁ and 12*k*₂, is visible at a dopant concentration as low as 0.3 moles per formula unit. While the total relative intensity of both the 12*k*₁ and 12*k*₂ sublattices is near 50%, a value consistent with BaFe $_{12}\text{O}_{19}$ or SrFe $_{12}\text{O}_{19}$ and indicative of a

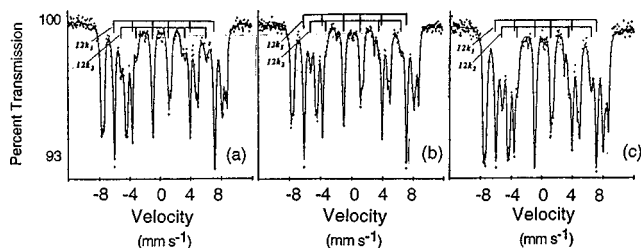


FIG. 1. ^{57}Fe Mössbauer spectra of doped SrFe $_{12-x}\text{M}_x\text{O}_{19}$ at 298 K. (a) M=In, $x=0.3$; (b) M=Ga, $x=0.3$; (c) M=Ga, $x=1.0$. Note the increase in the intensity of 12*k*₂ as x goes from 0.3 to 1.0 for Ga.

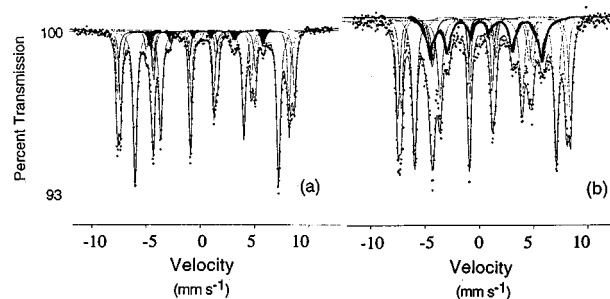


FIG. 2. ^{57}Fe Mössbauer spectra of (a) BaFe $_{11.75}\text{Sc}_{0.25}\text{O}_{19}$ and (b) a technical sample with a Sc content of 1.4 wt %. The 12*k*₂ subspectrum is highlighted. Note the substantially smaller 12*k*₂ field in comparison with those in Fig. 1.

lack of substitution of Ga, Sc, or In at the 12*k* site, it is clear that the 12*k*₁ intensity decreases while the 12*k*₂ intensity increases with increasing cation substitution.

Quite remarkably, the hyperfine fields of the 12*k*₁ and 12*k*₂ sublattices are insensitive to the degree of cation substitution between 0.3 and 1.0 mole per formula unit. There is, however, a strong dependence of the 12*k*₂ hyperfine field on the nature of the dopant. For the gallium substituted hexaferrites, the hyperfine field of the 12*k*₂ site is approximately 358 kOe. The scandium substituted hexaferrites have a remarkably lower 12*k*₂ field strength of approximately 320 kOe.

The virtually constant hyperfine fields for the 12*k*₁ and 12*k*₂ patterns may be rationalized on the basis of the presence of competing magnetic exchange interactions at the 12*k* site. Since the H_{eff} is proportional to the net exchange interactions at the site, the difference between the competing interactions at the 12*k* site must also be constant. The remarkable influence of scandium substitution may be attributed to the substitution of Sc on both the 4*f*₂ and the 2*b* site. This result suggests that the 2*b* site plays a critical role in determining the magnetic structures in hexagonal ferrites, an influence that is beyond that considered in existing models.

Finally, the influence of scandium substitution is also apparent in the technically relevant sample presented in Fig. 2. With increasing levels of substitution, a complex spectra results which is difficult to interpret in terms of traditional *M*-type magnetic structure.

¹P. Röschmann, M. Lemke, W. Tolksdorf, and F. Welz, Mater. Res. Bull. **19**, 375 (1984).

²J. R. Truesdow, K. D. McKinstry, R. Karim, and C. E. Patton, IEEE Trans. Magn. **28**, 3309 (1992).

³J. R. Truesdow, K. D. McKinstry, P. Kabos, and C. E. Patton, J. Appl. Phys. **74**, 2705 (1993).

⁴O. P. Aleshko-Ozhevskii and I. I. Yamzin, Sov. Phys. JETP **29**, 655 (1969).

⁵M. I. Namtalishvili, O. P. Aleshko-Ozhevskii, and I. I. Yamzin, Sov. Phys. Solid State **13**, 2137 (1972).

⁶G. K. Thompson, Ph.D. thesis, University of Michigan, Ann Arbor, MI, 1994.

⁷T. M. Clark, Ph.D. thesis, University of Michigan, Ann Arbor, MI, 1997.