

The structure–property relationships in M-type hexaferrites: Hyperfine interactions and bulk magnetic properties

G. K. Thompson and B. J. Evans

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

^{57}Fe Mössbauer spectroscopic measurements have been made at 296 K on single crystals of $\text{MFe}_{12}\text{O}_{19}$ ($\text{M}=\text{Ba}, \text{Sr}, \text{Pb}$) oriented parallel and perpendicular to the c axis, permitting the establishment of the systematics of the static and dynamical aspects of the hyperfine interactions, and their relationship to crystal/chemical structures for the five Fe^{3+} sublattices, and to the bulk magnetic properties. With the exception of the electric quadrupole interaction at the $2b$ site, and the dependence of the $2b$ intensity on the crystal orientation, the magnitude of the hyperfine interactions of a given Fe^{3+} site exhibits only small variations among the different hexaferrites. The magnitude of the quadrupole interaction at the $2b$ site varies by more than 10%, with the $2b$ site in $\text{PbFe}_{12}\text{O}_{19}$ exhibiting the smallest value. The relative intensity of the $2b$ subspectrum varies markedly among the three hexaferrites for observations parallel and perpendicular to the c axis. Although all display the expected anisotropy resulting from the libration of the $2b$ Fe^{3+} parallel to the c axis, the anisotropy is considerably larger for $\text{PbFe}_{12}\text{O}_{19}$ than for $\text{BaFe}_{12}\text{O}_{19}$ or $\text{SrFe}_{12}\text{O}_{19}$. It is remarkable that the bulk magnetic anisotropy follows the same order as the anisotropy in the dynamical displacement and crystalline electric field of the $2b$ site.

I. INTRODUCTION

The M-type hexaferrites, $\text{MFe}_{12}\text{O}_{19}$ ($\text{M}=\text{Ba}, \text{Sr}, \text{Pb}$), are an important class of ferrimagnetic oxides. Their magnetic properties make them excellent materials for use as permanent magnets, recording media, and as components in microwave and higher-frequency devices.

The structure of these ferrites may be considered to consist of alternating spinel ($\text{S}=\text{Fe}_6\text{O}_8^{2+}$) and hexagonal ($\text{R}=\text{MFe}_6\text{O}_{11}^{2-}$) layers. The O^{2-} ions exist as close-packed layers, with the M^{2+} substituting for an O^{2-} in the hexagonal layer. The Fe^{3+} ions are distributed in the interstitial spaces of the close-packed layers. Three of the Fe^{3+} sites are octahedral ($12k$, $4f_2$, and $2a$); one is tetrahedral ($4f_1$), and one is trigonal bipyramidal ($2b$).

In previous investigations, single-crystal ^{57}Fe Mössbauer spectroscopy and x-ray diffraction measurements were employed to investigate the dynamics of the $2b$ Fe^{3+} ion in $\text{BaFe}_{12}\text{O}_{19}$ (Refs. 1–5), $\text{SrFe}_{12}\text{O}_{19}$ (Refs. 3, 6–8), and $\text{PbFe}_{12}\text{O}_{19}$.^{9,10} However, quantitative and comparative data on the vibrational anisotropy of *all* the Fe^{3+} ions in the end-member hexaferrites, and on their respective hyperfine interaction parameters have been lacking.

Therefore, to determine what influence each of the five Fe^{3+} sites has on the bulk magnetic properties of the different $\text{MFe}_{12}\text{O}_{19}$ compounds, Mössbauer spectra have been obtained at 296 K for single crystals with the c axis parallel and perpendicular to the γ -ray propagation direction.

II. EXPERIMENT

^{57}Fe Mössbauer spectra were collected at 296 K for oriented single crystals of $\text{BaMn}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$, and $\text{PbFe}_{12}\text{O}_{19}$. The resulting hyperfine parameters have been compared with the parameters of polycrystalline $\text{BaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$, and $\text{PbFe}_{12}\text{O}_{19}$ reported in an earlier

study from this laboratory.¹⁰ The spectra were obtained and analyzed as described in detail in a previous report.¹¹ Electron microprobe analysis (EMPA) and x-ray powder diffraction were employed to determine the composition and purity of the samples.

III. RESULTS AND DISCUSSION

The spectra for the case in which the c axis is perpendicular to the γ -ray propagation direction are quite similar for all samples. A typical spectrum for this orientation, that of $\text{SrFe}_{12}\text{O}_{19}$, is shown in Fig. 1, along with the spectrum of a polycrystalline sample for comparison. The hyperfine parameters of all the single-crystal samples are listed in Tables I–III. In this orientation, except for $\text{SrFe}_{12}\text{O}_{19}$, the relative intensity of the $2b$ subspectrum for each of the samples is fairly close to the theoretical value of 2, where the $12k$ site has a normalized intensity of 12 (Tables I–III). For a given Fe^{3+} site, the hyperfine parameters exhibit, *with few exceptions*, no significant variations between the hexaferrites.

The first exception is the unusually large isomer shift of the $2a$ subspectrum of $\text{SrFe}_{12}\text{O}_{19}$, relative to the other hexaferrites (Tables I–III). This deviation may be due to the difficulty in resolving the $4f_1$ and $2a$ components. The *second exception* is in the high values of the quadrupole interaction of the $4f_1$ and $2a$ sites in $\text{BaMn}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$ (Fig. 2). These larger than normal quadrupole interactions may be due to Jahn–Teller distortions, which have been observed in polycrystalline $\text{BaMn}_x\text{Fe}_{12-x}\text{O}_{19}$.¹²

It is notable that, except for the $2b$ site, the electric quadrupole interactions in $\text{SrFe}_{12}\text{O}_{19}$ and $\text{PbFe}_{12}\text{O}_{19}$ are very similar for all the iron sites. The quadrupole interaction for the $2b$ site in $\text{SrFe}_{12}\text{O}_{19}$ is 2.28 mm s^{-1} , versus 2.00 mm s^{-1} for $\text{PbFe}_{12}\text{O}_{19}$. A comparison of the electric quad-

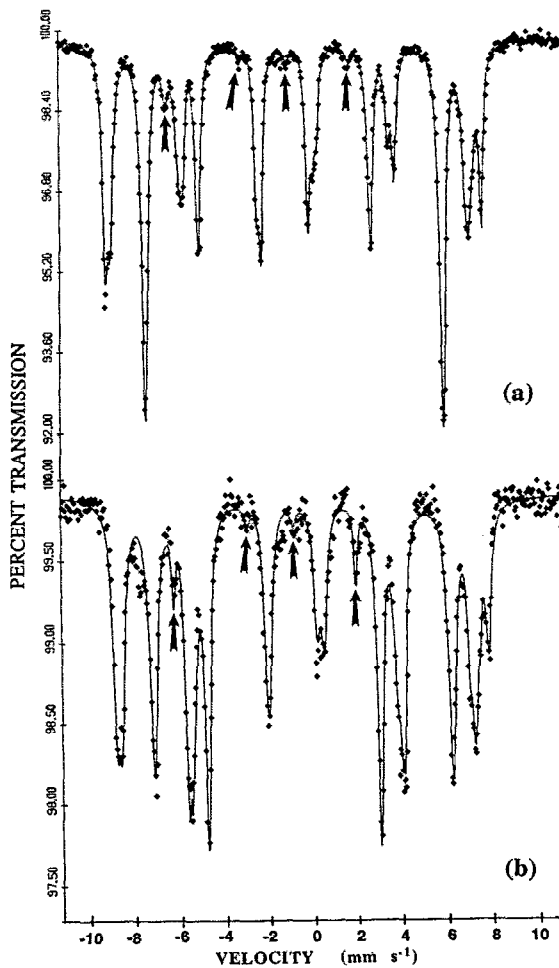


FIG. 1. (a) ^{57}Fe Mössbauer spectrum of polycrystalline $\text{SrFe}_{12}\text{O}_{19}$ at 296 K. (b) ^{57}Fe Mössbauer spectrum of single-crystal $\text{SrFe}_{12}\text{O}_{19}$ (c axis perpendicular to γ -ray beam) at 296 K. Arrows in (a) and (b) indicate the $2b$ subspectrum.

TABLE I. ^{57}Fe hyperfine parameters for single-crystal $\text{PbFe}_{12}\text{O}_{19}$ at 296 K.

Fe^{3+} site	Crystal alignment	H_{eff}^a (kOe)	Δ^a (mm s^{-1})	δ^a (mm s^{-1})	Relative intensity
12k	$c \perp \gamma$ -ray	412	0.35	0.33	12
	$c \parallel \gamma$ -ray	414	0.35	0.35	12
4f ₂	$c \perp \gamma$ -ray	513	0.29	0.39	4.9
	$c \parallel \gamma$ -ray	517	0.34	0.39	5.3
4f ₁	$c \perp \gamma$ -ray	494	0.11	0.30	4.4
	$c \parallel \gamma$ -ray	490	0.15	0.26	7.3
2a	$c \perp \gamma$ -ray	486	0.13	0.24	3.8
	$c \parallel \gamma$ -ray	505	0.06	0.36	3.2
2b	$c \perp \gamma$ -ray	398	2.00	0.30	2.2
	$c \parallel \gamma$ -ray	415	2.45	0.43	0.9

^aEstimated errors in H_{eff} , Δ , and δ (relative to Fe metal) are ± 1 kOe, ± 0.02 mm s^{-1} , and ± 0.01 mm s^{-1} , respectively.

TABLE II. ^{57}Fe hyperfine parameters for single-crystal $\text{SrFe}_{12}\text{O}_{19}$ at 296 K.

Fe^{3+} site	Crystal alignment	H_{eff}^a (kOe)	Δ^a (mm s^{-1})	δ^a (mm s^{-1})	Relative intensity
12k	$c \perp \gamma$ -ray	411	0.42	0.36	12
	$c \parallel \gamma$ -ray	410	0.51	0.34	12
4f ₂	$c \perp \gamma$ -ray	515	0.28	0.41	5.8
	$c \parallel \gamma$ -ray	511	0.57	0.43	4.9
4f ₁	$c \perp \gamma$ -ray	487	0.12	0.30	9.1
	$c \parallel \gamma$ -ray	503	0.47	0.28	4.1
2a	$c \perp \gamma$ -ray	501	0.13	0.34	2.2
	$c \parallel \gamma$ -ray	494	0.24	0.38	2.1
2b	$c \perp \gamma$ -ray	407	2.28	0.27	3.4
	$c \parallel \gamma$ -ray	412	0.95 ^b	1.03 ^b	1.7

^aEstimated errors in H_{eff} , Δ , and δ (relative to Fe metal) are ± 0.0 kOe, ± 0.02 mm s^{-1} , and ± 0.01 mm s^{-1} , respectively.

^bDue to the absence of the number 2 and 5 lines, these values are suspect.

rupole interaction in $\text{BaFe}_{12}\text{O}_{19}$ with that in $\text{SrFe}_{12}\text{O}_{19}$ and $\text{PbFe}_{12}\text{O}_{19}$ is problematic, due to the absence of crystal data. However, it is clear that the intrinsic quadrupole splitting for $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$ are quite similar, based on the similarity of the apparent values of the polycrystalline samples: 2.27 and 2.30 mm s^{-1} for $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$, respectively.¹⁰

Because the values of the *apparent* quadrupole interaction for the polycrystalline $\text{MFe}_{12}\text{O}_{19}$ samples are quite close to the *intrinsic* values for the crystals, it is clear that H_{eff} and the electric field gradient are collinear, as expected.

When the c axis is parallel to the γ -ray propagation direction, there are noticeable differences between the spectra of the different hexaferrites (Fig. 3). Although Mössbauer spectra of $\text{MFe}_{12}\text{O}_{19}$ in this orientation have been

TABLE III. ^{57}Fe hyperfine parameters for single-crystal $\text{BaMn}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$ at 296 K.

Fe^{3+} site	Crystal alignment	H_{eff}^a (kOe)	Δ^a (mm s^{-1})	δ^a (mm s^{-1})	Relative intensity
12k	$c \perp \gamma$ -ray	413	0.47	0.38	12
	$c \parallel \gamma$ -ray	411	0.52	0.36	12
4f ₂	$c \perp \gamma$ -ray	508	0.35	0.50	5.5
	$c \parallel \gamma$ -ray	509	0.48	0.44	5.8
4f ₁	$c \perp \gamma$ -ray	482	0.53	0.25	4.7
	$c \parallel \gamma$ -ray	485	0.45	0.30	7.1
2a	$c \perp \gamma$ -ray	497	0.37	0.31	3.1
	$c \parallel \gamma$ -ray	503	0.20	0.43	3.6
2b	$c \perp \gamma$ -ray	402	2.29	0.31	2.1
	$c \parallel \gamma$ -ray	0

^aEstimated errors in H_{eff} , Δ , and δ (relative to Fe metal) are ± 2 kOe, ± 0.02 mm s^{-1} , and ± 0.01 mm s^{-1} , respectively.

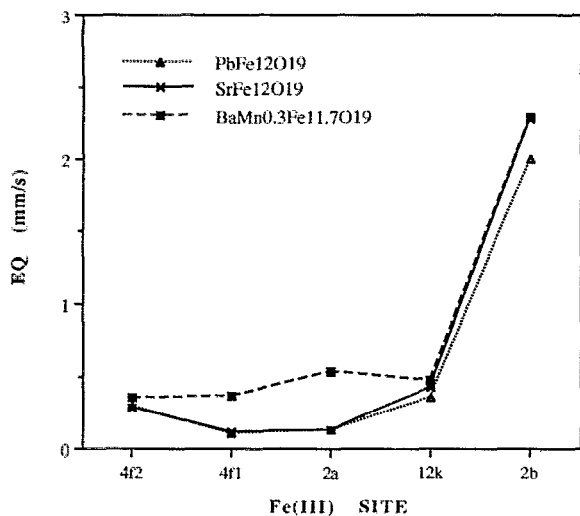


FIG. 2. Plot of Fe^{3+} site vs quadrupole interaction for $\text{MFe}_{12}\text{O}_{19}$ at 296 K (c axis perpendicular to γ -ray beam).

collected before, only now have quantitative differences been observed between the hexaferrites. It had previously been assumed that the hexaferrites exhibited similar anisotropies.

As is evident in Tables I and II, the relative intensity of the $2b$ subspectrum is clearly greater in $\text{SrFe}_{12}\text{O}_{19}$ than in $\text{PbFe}_{12}\text{O}_{19}$. This smaller relative intensity indicates that the $2b$ Fe^{3+} ion exhibits a significantly greater displacement parallel to the c axis in $\text{PbFe}_{12}\text{O}_{19}$ than in $\text{SrFe}_{12}\text{O}_{19}$. For the $\text{BaMn}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$ crystal, the low signal-to-noise ratio of the spectrum prevents any conclusions from being drawn about the displacement of the $2b$ Fe^{3+} ion in $\text{BaFe}_{12}\text{O}_{19}$. But based on the relative intensity of the $2b$ subspectra in the polycrystalline and perpendicularly oriented $\text{MFe}_{12}\text{O}_{19}$ samples, the $2b$ Fe^{3+} vibrational anisotropy of $\text{BaFe}_{12}\text{O}_{19}$ is expected to be very similar to that of $\text{SrFe}_{12}\text{O}_{19}$.

IV. CONCLUSION

Analysis of the ^{57}Fe Mössbauer hyperfine parameters for oriented single crystals have allowed the submicroscopic structure of the M-type hexaferrites to be related to their bulk magnetic properties. Only the $2b$ quadrupole interaction varies significantly between the three hexaferrites, suggesting that the oscillation parallel to the c axis of the $2b$ Fe^{3+} ion is the most important factor in determining the differences in their bulk magnetic behavior.

Based on the relative intensities of the $2b$ subspectra for crystals with the c axis parallel to the γ ray, a tentative ranking of the anisotropy in the displacement of the $2b$ Fe^{3+} ion in the $\text{MFe}_{12}\text{O}_{19}$ group can be inferred: $\text{PbFe}_{12}\text{O}_{19} > \text{SrFe}_{12}\text{O}_{19} \approx \text{BaFe}_{12}\text{O}_{19}$.

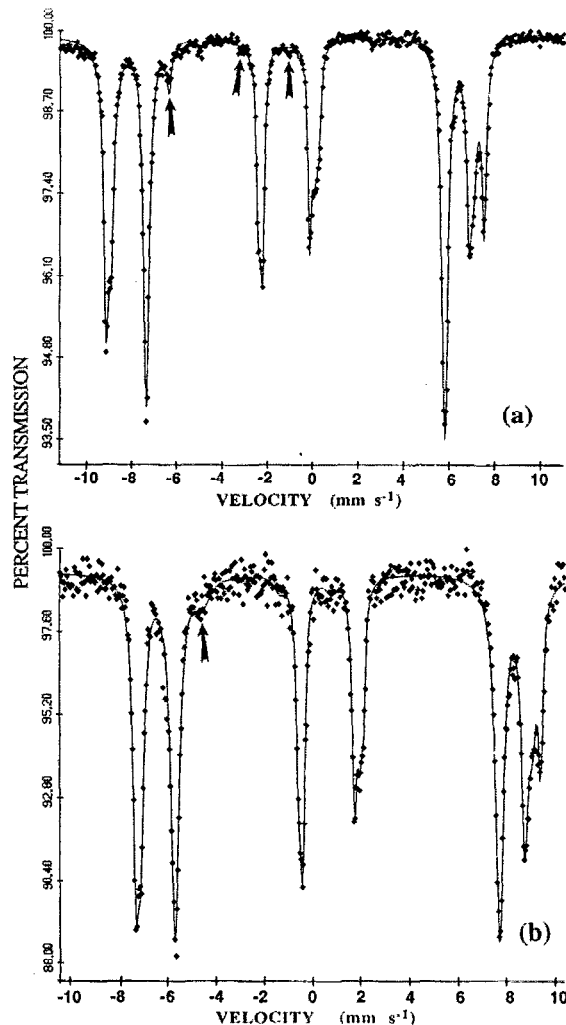


FIG. 3. (a) ^{57}Fe Mössbauer spectrum of single-crystal $\text{SrFe}_{12}\text{O}_{19}$ (c axis parallel to γ -ray beam) at 296 K. (b) ^{57}Fe Mössbauer spectrum of single-crystal $\text{PbFe}_{12}\text{O}_{19}$ (c axis parallel to γ -ray beam) at 296 K. Arrows in (a) and (b) indicate the $2b$ subspectrum.

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