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Letter to the Editor

^{57}Fe Mössbauer investigation of oriented single-crystal and polycrystalline $PbFe_{12}O_{19}$ *

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^{57}Fe Mössbauer spectra of $PbFe_{12}O_{19}$ have been obtained at 295 K on polycrystalline and single-crystal thin sections oriented with the *c*-axis parallel and perpendicular, respectively, to the γ-ray propagation direction. Due to the lower Néel temperature, the internal magnetic fields (H_{eff}) in $PbFe_{12}O_{19}$ are lower than those in $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ but the systematics of the hyperfine interactions are similar to those in other hexaferrites. For example, the relative values of H_{eff} exhibit the following sequence: $2b < 12k < 4f_1 < 2a < 4f_2$ and the isomer shifts (δ) exhibit the following ordering: $4f_1 < 2b \leq 2a \leq 12k < 4f_2$. The large dynamic displacement of the 2b Fe^{3+} ion parallel to the *c*-axis is clearly demonstrated by the relative intensity of the 2b site for the two oriented single crystals, being negligible for the crystal perpendicular to the *c*-axis, and equal to its population fraction for the crystal parallel to the *c*-axis. The lower value for the electric quadrupole splitting of the 2b site is believed to be related to the larger dynamic displacements at this site compared to other hexaferrites.

1. Introduction

With the recent determination of the structure of $PbFe_{12}O_{19}$ by single-crystal X-ray diffraction [1], it is now possible to examine by means of ^{57}Fe Mössbauer spectroscopy the magnetic properties of each of the end-member compositions of the magnetoplumbite-type hexaferrites, i.e., $SrFe_{12}O_{19}$ [2], $BaFe_{12}O_{19}$ [3] and $PbFe_{12}O_{19}$ and to perform a comparative and definitive analysis of the structure–property relationships among the three M-type hexaferrites.

Inasmuch as a complete set of Mössbauer parameters has not been reported for $PbFe_{12}O_{19}$ [4] and because of the considerable variation in hyperfine parameters reported for other hexaferrites [5], ^{57}Fe Mössbauer spectra have been obtained for $PbFe_{12}O_{19}$ polycrystalline and oriented single crystal samples at 295 K.

Despite the differences in their bulk magnetic properties, the ^{57}Fe hyperfine interactions of $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$ are similar in magnitude and exhibit similar systematics. Nonetheless, as a consequence of the lower Néel temperatures, the hyperfine fields of $PbFe_{12}O_{19}$ exhibit consistently the lowest values among the three hexaferrites. The origin of the lower values of the isomer shifts and quadrupole splittings for this phase is not so obvious.

2. Experimental

A single crystal specimen of $PbFe_{12}O_{19}$ was obtained from the Smithsonian Institution. This specimen was from the same batch of crystals from which specimens were taken for the single crystal X-ray study [1]. The stoichiometry previously reported [1] has been confirmed by independent electron microprobe analysis. Single crystal absorbers were prepared from slices cut both parallel and perpendicular to the basal plane of the single crystal. These slices were ground and polished to a thickness of approximately 20 μm. Fragments of the crystal were ground with an agate mortar and pestle to make the powder absorber.

* This article is dedicated to Professor Warren E. Henry, Emeritus Professor of Physics at Howard University, on his 80th birthday.

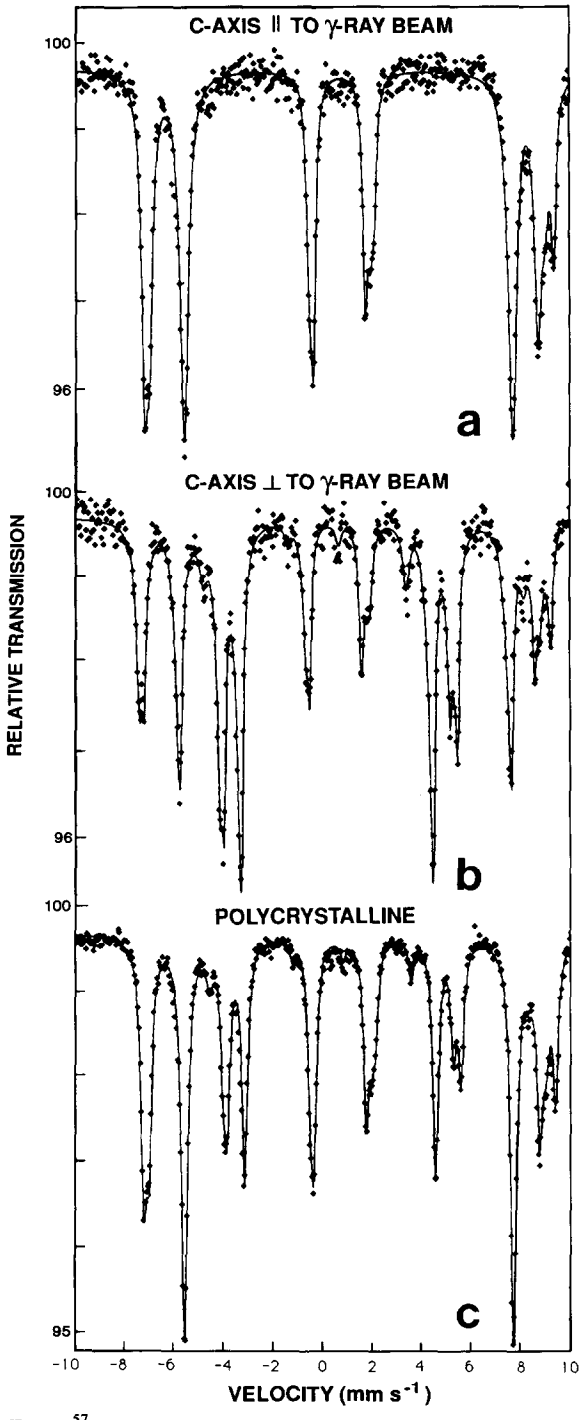

Fig. 1. ^{57}Fe Mössbauer spectra of single-crystal $PbFe_{12}O_{19}$ with (a) the *c*-axis parallel to the gamma ray beam, and polycrystalline $PbFe_{12}O_{19}$; (b) the *c*-axis perpendicular to the gamma ray beam; and (c) polycrystalline $PbFe_{12}O_{19}$. All spectra were obtained at 298 K.

The ^{57}Fe Mössbauer spectra for the single crystals were obtained with absorbers having their *c*-axis parallel and perpendicular, respectively, to the propagation direction of the γ-ray. The ^{57}Fe Mössbauer spectra were obtained and analyzed as described in detail in an earlier report [5].

3. Results and discussion

The ^{57}Fe Mössbauer spectra of the single-crystal and polycrystalline samples are shown in fig. 1. All spectra, except that for the single crystal with the *c*-axis parallel to the propagation direction of the γ-ray, exhibit the characteristic five iron subspectra, characteristic of the M-type hexaferrites.

The hyperfine parameters of the single-crystal and powder $PbFe_{12}O_{19}$ samples are listed in table 1. In the case of the crystal oriented with the *c*-axis perpendicular to the γ-ray, the relative intensity of the 2b site is 8.2%. This value is in good agreement with the theoretical relative intensity of 8.3%, which corresponds to the fraction of iron

Table 1
^{57}Fe hyperfine parameters for $PbFe_{12}O_{19}$ at 295 K

Iron site	Sample	H_{eff} [a] (kOe)	δ [a] (mm s^{-1})	Δ [a] (mm s^{-1})	Relative intensity
12k	⊥ single crystal [b]	413	0.33	0.35	12
	|| single crystal [b]	412	0.35	0.34	12
	powder	412	0.34	0.36	12
$4f_1$	⊥ single crystal	487	0.24	0.13	1.8
	|| single crystal	485	0.25	0.16	4.8
	powder	489	0.25	0.15	4.4
$4f_2$	⊥ single crystal	514	0.39	0.29	3.3
	|| single crystal	512	0.38	0.33	3.5
	powder	516	0.39	0.29	3.5
2a	⊥ single crystal	496	0.30	0.11	6.4
	|| single crystal	499	0.36	0.02	3.8
	powder	502	0.33	0.07	3.6
2b	⊥ single crystal	399	0.30	2.00	2.1
	|| single crystal	–	–	–	0
	powder	400	0.31	2.06	1.3

[a] Estimated errors in H_{eff}, δ (relative to Fe metal) and Δ are ±4 kOe, ±0.01 mm s^{-1} and ±0.05 mm s^{-1}, respectively.
[b] ⊥ single crystal and || single crystal are single crystals oriented with the *c*-axis perpendicular and parallel to the propagation direction of the γ-ray, respectively.

Table 2
Comparison of ^{57}Fe hyperfine parameters for polycrystalline $BaF_{12}O_{19}$ [a], $SrFe_{12}O_{19}$ [a] and $PbFe_{12}O_{19}$ samples

Iron site	Sample	H_{eff} [b] (kOe)	δ [b] (mm s^{-1})	Δ [b] (mm s^{-1})
12k	Ba [b]	414	0.35	0.76
	Sr [b]	414	0.35	0.61
	Pb	412	0.34	0.36
$4f_1$	Ba	492	0.31	0.40
	Sr	492	0.28	0.29
	Pb	489	0.25	0.15
$4f_2$	Ba	517	0.44	0.40
	Sr	518	0.40	0.38
	Pb	516	0.39	0.29
2a	Ba	511	0.45	0.20
	Sr	506	0.39	0.18
	Pb	502	0.33	0.07
2b	Ba	406	0.20	2.30
	Sr	411	0.31	2.27
	Pb	400	0.31	2.06

[a] $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ data are from ref. [5]. The spectra of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ were obtained at 300 K; the $PbFe_{12}O_{19}$ was at 295 K.
[b] Parameter errors are as in table 1.

ions occupying the 2b site. For the powder sample, the intensity of the 2b pattern is only 5.4% of the total. At the opposite extreme, the crystal with the *c*-axis parallel to the γ-ray propagation direction has a 2b pattern with a negligible intensity within the experimental error. These results are clear evidence of the strong, dynamic anisotropy in the displacements of the 2b Fe^{3+} ions. In comparison to $SrFe_{12}O_{19}$, the smaller relative intensity of the 2b site for $PbFe_{12}O_{19}$ suggests a larger displacement parallel to the *c*-axis for $PbFe_{12}O_{19}$.

For the purpose of comparisons, previously reported ^{57}Fe hyperfine parameters of polycrystalline $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ [4] and those for polycrystalline $PbFe_{12}O_{19}$ determined in their investigation are listed in table 2. The relative magnitudes of the parameters of lead hexaferrite follow the sample trends as that for the barium and strontium analogs. It is noteworthy that, with the exception of the 2b isomer shift, all of the $PbFe_{12}O_{19}$ hyperfine interaction parameters are less than those observed for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$.

The reported Curie temperatures T_c for single-crystal $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$ are 740, 750 and 725 K, respectively [6,7]. For materials with such similar crystal and magnetic structures and exchange interactions, the hyperfine fields should vary inversely with T/T_c. This is, indeed, the trend observed in table 2. With the exception of the 2a site, H_{eff} of $SrFe_{12}O_{19}$, which has the highest T_c, is equal to or greater than those for the corresponding site in $BaFe_{12}O_{19}$. For $PbFe_{12}O_{19}$, which has the lowest T_c, the hyperfine fields are consistently lower than those of either the Sr- or Ba-analogs.

4. Conclusions

The ^{57}Fe hyperfine parameters for $SrFe_{12}O_{19}$, $BaFe_{12}O_{19}$ and $PbFe_{12}O_{19}$ strongly suggest that there are few, if any, fundamental differences in their crystal/chemical structures and magnetic exchange interactions. There are some minor differences, however, that might have important consequences for some bulk properties. For example, the electric quadrupole splitting for the 2b site in $PbFe_{12}O_{19}$ is unexpectedly low; the intensity of this pattern also appears to be lower than that observed for either $SrFe_{12}O_{19}$ or $BaFe_{12}O_{19}$. Both of these results may be related to differences in the local structure of the 2b sites in the three materials [8].

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