

Mössbauer Study of Local Molecular Fields, Cation Distributions, and Recoilless Fractions in Sb-Substituted Lithium Ferrite

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Previous studies of the B -site hyperfine field distribution in spinel ferrites utilizing a local-molecular-field model have demonstrated that A -site cation disorder has a pronounced effect on $H_{\text{eff}}(B)$ and virtually no influence on $H_{\text{eff}}(A)$. The influence of B -site disorder on these hyperfine fields is less well known. We have made ^{57}Fe Mössbauer measurements on $\text{Li}_{1.2}\text{Fe}_{4.6}\text{Sb}_{0.2}\text{O}_8$ in which B -site disorder greatly predominates over A -site disorder. From the near natural linewidths for the A and B -site patterns we conclude that, in this material, B -site cation disorder is not nearly as effective as A -site cation disorder in producing inhomogeneities in H_{eff} at either site. The area ratio of the two hyperfine field patterns, which are well resolved in an applied field, yields equal recoilless fractions for the two sites.

The ^{57}Fe Mössbauer effect has recently been used¹⁻⁴ to study pure and substituted lithium ferrite, LiFe_5O_8 . Pure lithium ferrite has the spinel structure with all of the Li^{1+} ions occupying 25% of the octahedral B sites, and with Fe^{3+} occupying the remaining B sites and all of the tetrahedral A sites. For most spinel ferrites, with the notable exception of magnetite, the A - and B -site ^{57}Fe subspectra are not resolved sufficiently to permit an accurate determination of either their respective effective magnetic fields $H_{\text{eff}}(A)$ and $H_{\text{eff}}(B)$, or of the recoilless fraction ratio f_B/f_A . However, due to the ferrimagnetism of these materials, the application of an external magnetic field can often be used to resolve the two subspectra. Details of the spectra can then be studied more effectively. In this paper we present the results of a Mössbauer study of an antimony substituted lithium ferrite, $\text{Li}_{1.2}\text{Fe}_{4.6}\text{Sb}_{0.2}\text{O}_8$, in which an external field has been used to improve the resolution of the subspectra.

The polycrystalline sample was prepared according to a ceramic technique, identical to that described by Blasse.⁵ The sample was analyzed using x-ray diffraction techniques and wet chemical analyses. The analyzed composition corresponded to $\text{Li}_{1.196}\text{Fe}_{4.64}\text{Sb}_{0.206}\text{O}_8$ and the lattice constant was 8.345 Å, in good agreement with the previously reported value.⁵ In the substitution of Sb^{5+} for some of the B -site Fe^{3+} , using Li^{1+} for charge compensation according to the mechanism $\text{Fe}^{3+} + \text{Li}^{1+} = \text{Sb}^{5+}$, some Li^{1+} ions are driven onto A sites, which may produce non-negligible inhomogeneities in $H_{\text{eff}}(B)$. It is expected that the Mössbauer-effect spectra will show an effect on $H_{\text{eff}}(A)$ due to B -site disorder that is larger than that found in pure lithium ferrite. These results are of interest in elucidating the parameters in a local-molecular-field model^{2,6} for the magnetic structures in the spinel and garnet ferrites. The resulting cation distribution, as deduced from x-ray intensity and magnetization measurements⁵ on a similar specimen, is therefore $(\text{Li}_{0.14}\text{Fe}_{1.86}) [\text{Li}_{1.06}\text{Fe}_{2.74}\text{Sb}_{0.2}] \text{O}_8$. The cation

disorder is only 7% on the A site, while 31% of the B sites are occupied by diamagnetic ions. This distribution makes it possible for one to determine the effect on H_{eff} of a highly disordered B site in the presence of a negligible amount of A -site cation disorder. The reverse has generally been the case in previous investigations.⁷⁻¹⁰ Mössbauer spectra were obtained on equipment previously described.¹¹

A Mössbauer spectrum in an applied external field of 50 kG is shown in Fig. 1. The parameters resulting from a computer-assisted least-squares analysis of this spectrum and of a zero-field spectrum, in terms of two magnetic hyperfine spectra with Lorentzian line-shapes, are given in Table I. We also include for comparison purposes previous data⁴ on LiFe_5O_8 . We note that the least-squares fit to two (unresolved) hyperfine field patterns for the zero-field spectrum was only possible by using constraints on relative intensities as obtained from the applied magnetic field spectrum.

It is readily noticed (cf. Table I) that there is a systematic broadening of the outermost lines over the innermost lines. Although precise comparison is difficult, the broadening observed here is smaller than that observed for larger amounts of A -site disorder.^{2,7,9} Under identical experimental conditions, we have determined the width of the outermost lines of an Fe-metal spectrum to be 0.31 mm/sec. This width includes all instrumental broadening. Magnetic hyperfine spectra having widths greater than this can be interpreted as having inhomogeneities either in the quadrupole interactions or in the magnetic hyperfine interactions. The fact that the outermost lines are broadened to a greater extent than the innermost ones (with $\Delta\Gamma_1$ or $\epsilon \cong 6\Delta\Gamma_3$ or 4) shows that magnetic broadening² dominates in this material. The "excess" broadening $\Delta\Gamma$ of the outermost lines (lines 1 and 6) is 0.13 mm/sec for A -site and 0.27 mm/sec for B -site subspectra, respectively. (Thickness broadening of these lines is small and estimated to be less than 0.02 mm/sec.)

TABLE I. Parameters obtained from least-squares computer-aided fits to $\text{Li}_{1.2}\text{Fe}_{4.6}\text{Sb}_{0.2}\text{O}_8$ spectra (Fig. 1). Data for LiFe_2O_4 from Ref. 4.

Material	H_{ext} (kG)	Γ_A^a (mm/s)	Γ_A^b (mm/s)	Γ_B^a (mm/s)	Γ_B^b (mm/s)	$H_{\text{eff}}(A)$ (kOe)	$H_{\text{eff}}(B)$ (kOe)	$IS(A)^c$ (mm/s)	$IS(B)^c$ (mm/s)
$\text{Li}_{1.2}\text{Fe}_{4.6}\text{Sb}_{0.2}\text{O}_8$	0	0.46 ± 0.01	0.34 ± 0.01	0.53 ± 0.01	0.30 ± 0.01	515 ± 5	527 ± 5	0.240 ± 0.002	0.472 ± 0.002
$T = 100^\circ\text{K}$	49 ± 1	0.44 ± 0.01	0.33 ± 0.01	0.58 ± 0.01	0.36 ± 0.01	572 ± 5	481 ± 5	0.277 ± 0.002	0.406 ± 0.002
$\text{LiFe}_2\text{O}_4^d$	0		0.50 ± 0.05^d			508 ± 5^d		0.295 ± 0.050^d	
$T = 298^\circ\text{K}$	37 ± 1	0.34 ± 0.05	0.24 ± 0.02	0.39 ± 0.05	0.28 ± 0.05	536 ± 5	474 ± 5	0.334 ± 0.002	0.375 ± 0.002

^a Average width obtained for outermost lines (lines 1 and 6).

^b Average width obtained for innermost lines (lines 3 and 4).

^c With respect to a Fe-metal absorber.

^d Average width of outermost lines for two unresolved A and B patterns.

^e Data shown are for a sample of disordered LiFe_2O_4 .

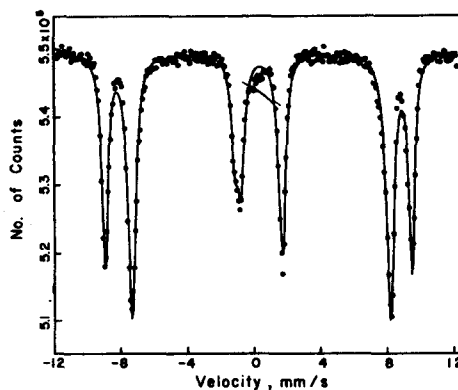


FIG. 1. Spectrum of $\text{Li}_{1.2}\text{Fe}_{4.6}\text{Sb}_{0.2}\text{O}_8$ at 100°K with an externally applied field of 49 ± 1 kG parallel to the direction of γ -ray propagation. The circles are data points and the solid line is a least-squares fit to two hyperfine field patterns (with lines 2 and 5 missing and assuming Lorentzian-shaped lines). The pattern with the largest hyperfine field is from the A-site Fe^{3+} ions aligned antiparallel to the applied field, and the pattern with smaller hyperfine field (but greater intensity) is from the B-site Fe^{3+} ions aligned parallel to the applied field. Deviation from the fit at the center of the spectrum is due to Fe present in Be counter windows (source moving).

If we assume that the multiplicity of fields at the A and B sites can be accounted for on the basis of a local-molecular-field model, including only nearest-neighbor interactions, we can have four different fields at the B site and nine different fields at the A site. The change in H_{eff} on the basis of this model is a linear function of one parameter ΔH_{eff} multiplied by the number of diamagnetic neighbors a given Fe^{3+} ion has among its nearest-neighbor cations on the opposite sublattice. Then, assuming a random distribution on each sublattice, and using $\Delta H_{\text{eff}}(A)$ and $\Delta H_{\text{eff}}(B)$ as additional variable parameters in the least-squares computer fit, we obtain for these parameters the values -4 and -17 kG, respectively, and a statistically significant improvement in the goodness of fit. The improvement in fit was visible as a reduction in the discrepancy for the least-squares fit to the outermost lines obvious in Fig. 1. The value obtained here for $\Delta H_{\text{eff}}(B)$ compares closely with those of -20 and -12 kG obtained for CoFe_2O_4 and CuFe_2O_4 , respectively.^{7,10} There have been no previous measurements of $\Delta H_{\text{eff}}(A)$. Therefore, we find quantitative evidence that B-site cation disorder is not nearly as effective as A-site cation disorder in producing inhomogeneities in H_{eff} . It appears that the strength of A-site cation disorder is approximately four to five times as large as B-site cation disorder in producing inhomogeneities in H_{eff} of the oppositely oriented sublattice.

The complete absence of any absorption in the region where lines 2 and 5 would appear in Fig. 1 shows that, in spite of the large concentration, $\sim 30\%$, of diamagnetic ions on the B sites, $\text{Li}_{1.2}\text{Fe}_{4.6}\text{Sb}_{0.2}\text{O}_8$ has a collinear, antiparallel Néel spin structure.

The difference of 0.13 mm/sec between the *A*- and *B*-site isomer shifts (IS), $IS(B) - IS(A)$, is in good agreement with that observed in other spinel ferrites.^{2,4,12} The somewhat larger absolute magnitudes are due to the difference between the source and absorber temperatures. The magnitude of the *apparent* quadrupole splitting is equal to zero within our experimental error, as is also the case⁴ for $LiFe_5O_8$.

Since our synthesis technique, x-ray diffraction, and chemical analyses were very similar to those of Blasse,⁶ we may assume that the cation distribution is as determined by Blasse,⁶ and a comparison of the areas for the two hyperfine field patterns of Fig. 1 can be used, after a small correction for finite thickness,¹³ to determine the recoilless fraction ratio f_B/f_A . We find $f_B/f_A = 0.99 \pm 0.01$ at 100°K. This ratio is consistent with the value 1.0 found⁴ for $LiFe_5O_8$ at 298°K and 0.99 found¹³ for magnetite at 4°K and offers additional evidence that the cation distribution deduced from the magnetization and x-ray intensity data⁶ is correct.

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Magnetic Structures of Tb_2C_3 and Ho_2C_3 *

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Tb_2C_3 and Ho_2C_3 are isostructural (the cubic body-centered Pu_2O_3 -type structure), but neutron diffraction revealed markedly different ordered spin configurations. In Tb_2C_3 below 33°K, two out of four body-diagonal linear Tb arrays become individually a one-dimensional antiferromagnetic chain, but the remaining two arrays show no ordered spins at all. The nearest Tb atoms between the different ordered arrays are ferromagnetically coupled. The moment direction lies most likely along a face diagonal and the saturation moment is essentially equal to the free ion value of 9 Bohr magnetons. In Ho_2C_3 , below 19°K, two out of four linear Ho arrays become ferromagnetic and the remaining two undergo antiferromagnetic ordering. Among three closest Ho–Ho approaches linking the different linear arrays, two pairs are antiferromagnetically related and the remaining pairs are ferromagnetically coupled. The moments are directed along one of the ferromagnetic arrays and the saturation moment is 7.3 Bohr magnetons which is considerably smaller than the free ion value of 10 Bohr magnetons. The energy levels due to a highly asymmetric crystal field should at least partly be responsible for the differences between the Tb_2C_3 and Ho_2C_3 spin structures. Both the magnetically long-range ordered Tb_2C_3 and Ho_2C_3 exhibit a sizeable, magnetic diffuse scattering having the characteristics of ferromagnetic short-range order.

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