SUPERTRANSFERRED HYPERFINE FIELDS AT Sb^{5+} IN INSULATING FERRITES: EFFECTS OF LOCAL ORDER AND ION-SPECIFIC PROPERTIES

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ABSTRACT

The supertransferred hyperfine fields at Sb^{5+} in $LiFe_5O_8$, $CoFe_2O_4$, and YIG have been determined using ^{121}Sb Mössbauer spectroscopy. In contrast to $CoFe_2O_4$, $NiFe_2O_4$, and YIG, the small, average hyperfine field of ~ 100 kOe at Sb^{5+} in $LiFe_5O_8$ requires the existence of significant local order and indicates that the clustering of Li^{1+} about Sb^{5+} is approximately ten times as large as that expected for a random intrasite cation distribution, in agreement with the known strong influence of Sb substitution in destroying the Li:Fe ordering. The decrement in the hyperfine field at Sb^{5+} due to an A-site Co^{2+} is also found to be larger than that due to Ni^{2+}.

INTRODUCTION

As a part of a continuing effort to establish the systematics of supertransferred hyperfine fields (STHF) at diamagnetic cations in insulating ferrites,[1] ^{121}Sb Mössbauer measurements have been made for Sb^{5+} substituted $CoFe_2O_4$, $LiFe_5O_8$, and $Y_3Fe_5O_{12}$(YIG) and are compared with previous measurements on Sb^{5+} and Sn^{4+} in other ferrites.

First of all, the general trends in the previously reported studies[1] have been further confirmed. Secondly, the assumption of random cation distributions-- an assumption commonly made in applying microstatistical considerations to STHFs-- is found to be a poor description of the actual Li^{1+} intrasite distribution in Sb substituted $LiFe_5O_8$. Evidence for the influence of the specific details of the spin and electron density distributions of neighboring ions on the STHF is found in the different effects of Ni^{2+} and Co^{2+} on the STHF at Sb^{5+} .

EXPERIMENTAL

All of the samples were prepared according to the prescriptions of Blasse.[3] They were characterized using x-ray powder diffractometry and wet-chemical analytical techniques. All of the samples were single-phase and the analyzed compositions are given in Table I. The Mössbauer spectrometer, data collection and analysis techniques were identical to those described in detail previously.[1,2]

RESULTS

The spectra of the different samples at 100 K are shown in Fig. 1. From our experience with other Sb substituted ferrites,[1,2] it was obvious that all of the samples, except YIG, had a distribution of hyperfine fields at the Sb^{5+} ion. Therefore, the spinel ferrite spectra were fitted to a magnetic-plus-electric quadrupole pattern, with the addition of an assumed Lorentzian distribution of hyperfine fields about some mean value H_{sthf}. The width (FWHM) of the hyperfine field distribution, Γ_{sthf}, was one of the fitted parameters. The solid lines in Fig. 1 are the results of a least mean-squares fit of these assumptions to the spectra. The parameters from these fits are given in Table I. The electric quadrupole interactions were found to be negligibly small and are not listed in Table I.

Fig. 1. ^{121}Sb Möss-
bauer spectra at 100 K
for: (a)
$Y_{2.9}Ca_{0.2}Fe_{4.9}Sb_{0.1}O_{12}$,

(b) $Co_{1.1}Fe_{1.85}Sb_{0.1}O_4$,

(c) $Li_{1.2}Fe_{4.6}Sb_{0.2}O_8$.
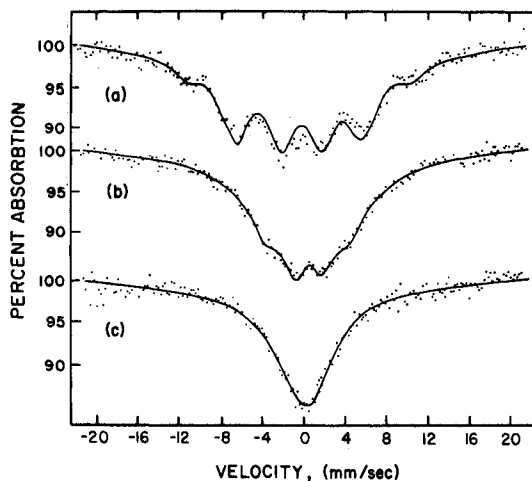
DISCUSSION

With the possible exception of Sb substituted $LiFe_5O_8$, the ^{121}Sb Mössbauer spectra of Fig. 1 evince appreciable magnetic hyperfine fields, as in other ferrimagnetic spinels and garnets.[1,2,4] Even though there is

no resolved splitting in the spectrum of Sb substituted $LiFe_5O_8$ (Fig. 1c), the width of an assumed single-line would be ~7 mm/sec and three times that expected for an intrinsic, single-line [121]Sb pattern.[2] The possibility of large, unresolved quadrupole splitting can be dismissed since the electric quadrupole interaction has been found to be small in a variety of different spinel ferrites;[2] the spectrum also lacks the expected asymmetry which accompanies a large electric quadrupole splitting.

Table I. [121]Mössbauer parameters at 100 K of Sb substituted ferrites. $\langle H_{sthf} \rangle$ is the average value of an assumed Lorentzian distribution of hyperfine fields and Γ_{sthf} is the width (FWHM) of this distribution. Individual lines were assumed to have Lorentzian profiles and relative widths and intensities for a thin absorber.

Sample (Actual Compositions)	$\langle H_{sthf} \rangle$ (kOe)	Γ_{sthf} (kOe)	Isomer Shift[a] (mm/sec)
$Li_{0.60}Fe_{2.30}Sb_{0.11}O_4$	116(3)	149(10)	-0.2(1)
$Co_{1.10}Fe_{1.82}Sb_{0.06}O_4$	172(2)	63(6)	-0.6(1)
$Co_{1.21}Fe_{1.68}Sb_{0.12}O_4$	165(2)	60(6)	-0.6(1)
$Y_{2.9}Ca_{0.2}Fe_{4.9}Sb_{0.1}O_{12}$	267(5)	--	-0.1(1)

[a]w.r.t. $BaSn(Sb)O_3$ at 100 K

Since our samples were prepared in a manner identical to that of Blasse,[3] we may reasonably assume them to have very similar cation distributions. Sb^{5+} is located exclusively on the octahedral sites in every case. 6% of the A sites are occupied by Li in $Li_{0.6}Fe_{2.3}Sb_{0.1}O_4$; 26% of the A sites are occupied by Co in $Co_{1.2}Fe_{1.7}Sb_{0.1}O_4$; and the cation is not accurately known for $Co_{1.1}Fe_{1.85}Sb_{0.05}O_4$ but is assumed to be similar to that for pure $CoFe_2O_4$. In all of these materials except YIG, the Sb^{5+} ion has chemical and magnetic disorder among next-nearest-neighbor (NNN) cation environments.

If the value of the magnetic hyperfine field at Sb^{5+} in $CoFe_2O_4$ and $LiFe_5O_8$, having only A site Fe neighbors, is assumed to be the same as that in $NiFe_2O_4$,[2] we obtain values of 80 kOe and 400 kOe, respectively, for the decrement, ΔH, in the magnetic hyperfine field per non-Fe A site neighbor. These ΔH values differ from that of 50 kOe as found for $NiFe_2O_4$. While the differences between the ΔH values of 50 kOe for Sb^{5+} and 30 kOe for Sn^{4+} in YIG are believed to understood qualitatively, the results reported here for Sb^{5+} in $CoFe_2O_4$ and $LiFe_5O_8$ are not explicable in terms of the general systematics of [121]Sb

STHFs; and a consideration of the dominance of effects unique to the Co^{2+} and Li^{1+} ions and/or local structural details might be instructive.

Recent studies of the STHF at ^{57}Fe in $Co_{1-x}Zn_xFe_2O_4$[5] have shown that the ΔH associated with substituting Co for Fe on an A site has a value somewhat larger than that due to a diamagnetic cation such as Zn and also larger than that due to Ni.[2] If we assume a similar behavior for Co^{2+} on the STHF at Sb^{5+}, then the larger value of ΔH for Co^{2+} relative to that for Ni^{2+} is to be expected.

The small difference in the magnitudes of $\langle H_{sthf} \rangle$ and Γ_{sthf} for $Co_{1.1}Fe_{1.85}Sb_{0.05}O_4$ and $Co_{1.2}Fe_{1.7}Sb_{0.1}O_4$ (cf. Table I) vis-à-vis the diferences between these parameters for $Ni_{1.1}Fe_{1.85}Sb_{0.05}O_4$ and $Ni_{1.2}Fe_{1.7}Sb_{0.1}O_4$[2] follows directly from the small differences in the A site cation distributions for these two compositions of cobalt ferrites. The fractional occupation of the A sites by Co^{2+} in $Co_{1.1}Fe_{1.85}Sb_{0.05}O_4$ is at least 0.22,[5] and it increases by only 4% to 0.26 in $Co_{1.2}Fe_{1.7}Sb_{0.1}O_4$.[3]

In view of the small variations in the value of the STHF at Sb^{5+} in a variety of ferrites for a given local environment, the unusually small value of 100 kOe for $\langle H_{sthf} \rangle$ and large value of ~400 kOe for ΔH at Sb^{5+} in $LiFe_5O_8$ are anomalous. However, in arriving at this value for ΔH a random, intrasite distribution of Li^{1+} ions on the A site s was assumed. There is reason to believe that this assumption is not correct. Blasse[3] has shown that Sb substitution in $LiFe_5O_8$ is quite effective in destroying the 1:3 Li-Fe ordering on the B site. Presumably, the disordering involves local clustering of Li^{1+} ions about the Sb^{5+} ions. Such clustering would involve Li^{1+} ions on both the A and B sites. Therefore, the number of Li^{1+} A-site ions that are NNN to a B-site Sb^{5+} ion is much greater than that expected on the basis of a random intrasite distribution of Li^{1+}. Once local clustering of Li^{1+} about Sb^{5+} is taken into account, the smaller value of $\langle H_{sthf} \rangle$ for Sb^{5+} in $Li_{1.2}Fe_{4.6}Sb_{0.2}O_8$ relative to that in $Ni_{1+2x}Fe_{2-3x}Sb_xO_4$ and $Co_{1+2x}Fe_{2-3x}Sb_xO_4$ is found to be qualitatively consistent with the systematics of STHFs at diamagnetic cations in spinel ferrites. Using previously developed data analysis techniques,[2] the average number of A site Li^{1+} ions that are NNN to a Sb^{5+} ion is estimated to be ~4. This estimate was arrived at by employing a value of 50 kOe for ΔH and 300 kOe for H_{sthf} at a Sb^{5+} ion having only Fe A-site NNN. This result is to be compared with an average number of 0.4 Li^{1+} A-site ions about a Sb^{5+} ion expected for a random intra-site distribution of tetrahedral Li^{1+} ions in $Li_{1.2}Fe_{4.6}Sb_{0.2}O_8$.

The ^{121}Sb Mössbauer spectrum of Sb^{5+} in YIG was reported by other investigators[6] shortly after we completed

our measurements. However, our sample composition is different from that of $Y_{2.5}Ca_{0.5}Sb_{0.25}Fe_{4.75}O_{12}$ reported on in the earlier study.[6] We obtain 267 kOe for the STHF at Sb^{5+} in $Y_{2.8}Ca_{0.2}Sb_{0.1}Fe_{4.9}O_{12}$ which is less than that of 290 kOe obained for Sb in $Y_{2.5}Ca_{0.5}Sb_{0.25}Fe_{4.75}O_{12}$. We can offer no explanation for the apparent discrepancy since the saturation value of the STHF is expected to be similar for these two materials.[2] In agreement with the known cation distribution in Sb-substituted YIG and the fact that the tetrahedral neighbors of a given Sb ion are all Fe ions, the ^{121}Sb Mössbauer spectrum shown in Fig. 1a can be adequately fitted with a single hyperfine field.

CONCLUSION

In conclusion, we note that our previous prediction[1] of the relative magnitudes of the STHFs at ^{121}Sb and ^{119}Sn in YIG has been verified[6] and that our interpretaion of the predominance of 5s covalent charge transfer to the supertransferred hyperfine interaction mechanisms seems to be firmly established for Sb^{5+} and isoelectronic Sn^{4+}. Further refinements in our understanding of the systematics of STHFs at Sb^{5+} and Sn^{4+} will require careful consideration of the chemical bonding properties and magnetic exchange interactions specific to each ion as well as a knowledge of the local and possibly non-random cation distributions.

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