Supertransferred Hyperfine Fields and Covalency at Diamagnetic Cations in Magnetic Insulators

B. J. Evans*

Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan 48104

and

L. J. Swartzendruber

Institute for Materials Research, National Bureau of Standards, Gaithersburg, Maryland 20760

The sign and magnitude of the antimony hyperfine field has been measured in Sb-substituted nickel ferrite using the ^{121}Sb Mössbauer effect. We obtain a value of -311 ± 4 kG for this field at 100 K. This result is compared with results obtained for Sn in yttrium iron garnet and, among the possible mechanisms, $3d$-$5s$ covalent spin transfer appears to make the predominant contribution to the hyperfine field.

INTRODUCTION

It is well established that in order to account for the magnetic properties of paramagnetically ordered "ionic" salts, one must allow for (i) some overlap of the ligand electron wave functions with those of the magnetic electrons on the cations, (ii) some charge transfer from the ligand to the magnetic cation, and (iii) consequently, some spin transfer from the magnetic cation to the ligands.[1-5] The mechanisms of cation-ligand nearest-neighbor (nn) spin transfer have been investigated both theoretically and experimentally.[6,7] Recently, the importance of cation-cation interactions, both direct and via an intervening anion, to the spin-transfer process has been emphasized.[8] There are some unanswered and rather basic questions, though, regarding the contributions of these cation-cation interactions to the transferred and supertransferred hyperfine fields at the magnetic cations.[9,10] The ambiguity is due primarily to the smallness of the transferred fields relative to those produced by the cation's own unpaired electrons.[10] In addition, charge transfer and overlap act cooperatively in producing unpaired spin density at the anion site, whereas these processes act competitively at the magnetic cation site. Since the hyperfine fields at the nuclei of diamagnetic cations will be due almost entirely to that arising from supertransfer processes (except for a small dipolar field of the order of 10 kG), studies of "supertransferred hyperfine fields" (STHF) at nominally diamagnetic cations should be quite useful in determining the relative importance of the various mechanisms of spin transfer for the case of magnetic cations.

We report here the observation of the magnitude and sign of the magnetic hyperfine field at ^{121}Sb in antimony-substituted nickel ferrite, e.g., $Ni_{1.2}Fe_{1.7}Sb_{0.1}O_4$. This is the first instance to our knowledge in which the sign of the magnetic hyperfine field at ^{121}Sb has been determined using Mössbauer spectroscopy. The results are found to closely parallel those for Sn^{4+} in garnets.[11] Contrary to some recent studies, which concluded that the hyperfine field at Sn^{4+} in yttrium iron garnet (YIG) is related to the net macroscopic magnetization,[12] we find that the relative magnitudes and signs of the hyperfine fields at nominally diamagnetic Sn^{4+} in YIG and Sb^{5+} in $NiFe_2O_4$ can be best understood on the basis of a local next-nearest-neighbor (nnn) $3d$-$5s$ covalent-spin-transfer mechanism via the covalence of the metal-ligand bonds. While overlap effects are also found to be important, possibly accounting for as much as 50% of the total hyperfine field, the difference in the magnitudes of the fields at Sn^{4+} and Sb^{5+} is due to the greater covalence (charge transfer) in the Sb^{5+}-O^{2-} bonds than in the Sn^{4+}-O^{2-} bonds.

Recently, large magnetic hyperfine fields have been observed at the nuclei of nominally diamagnetic Sn^{4+} and Sb^{5+} ions in ferrimagnetic garnets and spinel ferrites, respectively.[11-13] The magnitudes of these hyperfine fields suggest substantial spin transfers. Since it has been shown that the strength of the superexchange interactions is determined by the amount of covalent spin transfer, it would appear that the Sn^{4+} and Sb^{5+} ions have considerable influence on the magnetic exchange interactions in these materials. At present, little is known regarding the role of the nnn diamagnetic cations in the exchange interactions in magnetically ordered insulators. It has been noted, nonetheless, that the bulk magnetic properties, e.g., T_C, T_N, and sublattice magnetizations of many garnet, spinel, and perovskite oxides containing nominally diamagnetic cations are inexplicable if it is assumed that the diamagnetic cations play no *direct* role in the magnetic exchange interactions.[14-16] YIG : Sn and $NiFe_2O_4$: Sb do not constitute the first instances in which a magnetic hyperfine field has been ob-

served at a diamagnetic cation in a magnetic insulator, since hyperfine fields have also been observed[17-20] at Ga in YIG, at P in $LiMnPO_4$, at Co^{3+} in Co_3O_4, and at La^{3+} in $La_{0.7}Sr_{0.3}MnO_3$. However, with the possible exception of Ga in YIG,[17] the magnitudes of the fields have never approached those observed at Sn^{4+} and Sb^{5+} in YIG and $NiFe_2O_4$, respectively. Indeed, the hyperfine fields at each of these ions in these materials are either as large as, or greater than, those observed in ferromagnetic alloys and metals in which the Sb and Sn atoms are nearest neighbors to magnetic ions.[21,22]

At the present state of development of the theory of supertransferred hyperfine interactions, some fundamental questions remain concerning the mechanisms which transfer spin density from the magnetic cations to the diamagnetic cations and, for that matter, whether there is a "transfer" of spin density at all, either directly or via an intervening anion. It does not appear that overlap considerations alone can lead to the degree of net spin polarization required to produce the observed hyperfine fields at Sn^{4+} and Sb^{5+}. We shall show that most of the unpaired spin density on the diamagnetic ions, at least in the cases considered here, is due to spin transfer (assisted by charge transfer) into the empty $5s$ orbital via the covalence of the metal-ligand bonds. One can reach a decision concerning the relative contributions of core-electron spin polarization via overlap and spin transfer via extended covalence (involving three-center molecular orbitals) by determining the sign of the hyperfine fields. This explanation provides a qualitative understanding of the influence of these nominally diamagnetic cations on the bulk magnetic properties of the spinel, garnet, and perovskite magnetic insulators.

EXPERIMENTAL

The ^{121}Sb Mössbauer spectra were obtained by means of a constant-acceleration fly-back-type spectrometer mounted above a 50-kG superconducting magnet system. The source was 0.25 mCi of ^{121}Sn in $BaSnO_3$. The escape peak of the 37-keV γ ray in a Xe : CH_4-filled proportional counter was used to monitor the transmission of the γ ray as a function of velocity.[23] Both the source and absorber were cooled to 100 K. For the spectra obtained in the applied magnetic field, the source was in a field of approximately the same magnitude as that at the absorber. This was necessary in order to obtain a sufficient count rate with the low source intensity available. The presence of a magnetic field at the source produces more complex spectra than would a single-line source. However, for a ^{121}Sb source in a 50-kG field, the major effect on a spectrum obtained with an absorber having a much higher spontaneous field is to lead to line

broadening. Hence, the determination of the sign of the spontaneous internal field is still straightforward. In order to obtain the best possible signal-to-noise ratio, the region of the spectrum to be scanned was restricted to the absorption lines between ±8 mm/sec. The spectra were analyzed using computer techniques described previously.[24,25]

The specimen used in this study is identical to that employed in previous measurements.[11,26] Fe_2O_3, Sb_2O_3, and $NiCO_3$ were carefully weighed out in amounts corresponding to the stoichiometry $Ni_{1.2}Fe_{1.7}Sb_{0.1}O_4$. The resulting powder was then ground in the form of an acetone slurry into an intimate mixture using an agate mortar and pestle. The slurry was then dried, pelletized, and fired at 1150 K in a streaming atmosphere of dry oxygen, according to the prescription of Blasse.[27] This initial firing was followed by repeated grinding, pelletizing, and firing in an oxygen atmosphere until a single spinel-phase material was obtained. Attempts to obtain a more highly ordered specimen by slow cooling always resulted in the precipitation of Sb_2O_3. The specimen was analyzed using wet chemical analyses and powder x-ray diffraction. Using Mn-filtered Fe radiation, a Si internal standard, and a Philips powder diffractometer, the lattice constant was determined to be 8.359 Å, in good agreement with the value reported by Blasse.[27] Only the Ni and Fe concentrations were determined by means of the wet chemical analysis. The Ni and Fe concentrations were determined to be 30.0 and 39.0 wt%, respectively. The calculated concentrations for the desired composition are 29.16 wt% for Ni and 39.30 wt% for Fe, indicating a negligible deviation of the composition of the final product from that corresponding to $Ni_{1.2}Fe_{1.7}Sb_{0.1}O_4$.

RESULTS

In order to clarify discussion of the results, it is useful to first give the salient features of the crystal structure. In cubic spinel ferrites, the oxygen atoms form an fcc sublattice. Each unit cell contains 32 oxygen atoms with 96 interstitial sites, 32 of which are octahedrally coordinated and 64 of which are tetrahedrally coordinated. One-half of the octahedral sites are occupied (termed the "B" sites), and one-eighth of the tetrahedral sites are occupied (termed the "A" sites). Each B site is joined to six A sites via six metal-oxygen bonds with an A-O-B angle of ~125°, and also to six B sites with a 90° B-O-B angle. Each A site is joined to three other B sites through a single oxygen ion. In most spinels, there is also a lowering of the local symmetry of the B sites to D_{3d} due to a distortion of the oxygen sublattice. In $NiFe_2O_4$, the B sites are occupied randomly by both Ni^{2+} and Fe^{3+} ions and the A sites are occupied exclusively by Fe^{3+} ions, i.e., $NiFe_2O_4$ is an inverse spinel.

The magnetic structure is ferrimagnetic, with the B-site moments antiparallel to the A-site moments and the resultant moment parallel to the moments on the B sites. In Sb-substituted $NiFe_2O_4$ (i.e., $Ni_{1+2x}Fe_{2-3x}Sb_xO_4$), the Sb^{5+} ions are located only on the B sites.[27] The antiferromagnetic A-B exchange interactions are weakened by their presence, decreasing the Néel temperature with increasing Sb content. In addition, an amount y (which is slightly less than x) of Ni^{2+} is driven onto the A sites, which also serves to decrease the Néel temperature (the Ni^{2+}-Ni^{2+} A-B interactions are much weaker than the Ni^{2+}-Fe^{3+} and Fe^{3+}-Fe^{3+} interactions). The specimen used in this study has a cation distribution of $(Ni_{0.08}Fe_{0.92})$ $[Ni_{1.02}Fe_{0.88}Sb_{0.1}]O_4$, where ( ) and [ ] indicate A and B sites, respectively.

It has been shown previously that in Sb-substituted $NiFe_2O_4$, antimony nuclei differing in their nnn A-site environments experience magnetic hyperfine fields H_{eff} of different magnitudes.[11,23] The origin and quantitative aspects of this distribution in H_{eff} at ^{121}Sb were also established.[11,23] For example, it was found that the hyperfine field at Sb^{5+} was determined primarily by the magnetic moments of the nnn A-site ions (reminiscent of the systematics of the superexchange interactions in spinel ferrites). For the particular sample composition chosen for the present investigation, the smallness of the width of the distribution in the magnitudes of H_{eff} and the intensity of the spectrum have been optimized.

Assuming a random distribution of Sb^{5+} ions on the B sites, the magnetic hyperfine patterns of Sb nuclei having different nnn A-site environments were assigned fields and relative intensities according to the following relationships:

$$H_{eff}(n) = H_{eff}(0)\frac{1}{6}(6-n), \quad n = 0, 1, \ldots \quad (1)$$

$$I(n) = \binom{6}{n}(1-y)^{6-n}y^n, \quad n = 0, 1, \ldots \quad (2)$$

where $H_{eff}(0)$ is the magnetic hyperfine field at a ^{121}Sb nucleus that has no Ni^{2+} ions among its nnn A-site cations; $H_{eff}(n)$ is the magnetic hyperfine field at a Sb nucleus that has a total of n Ni^{2+} and $(6-n)$ Fe^{3+} ions among its nnn A-site cations; $I(n)$ is the relative intensity of the Mössbauer pattern corresponding to $H_{eff}(n)$; and y is the fraction of A sites occupied by Ni^{2+} (which is slightly less than the amount of added antimony). Fitting the Mössbauer spectra using the relationship $H_{eff}(n) = H_{eff}(0)$ $-n\Delta H_{eff}$ gave the same results as Eq. (1), i.e., $\Delta H_{eff} = 52$ kG. From the symmetry of the spectra, it is known that the electric quadrupole splitting is negligibly small for all of the patterns and also that the isomer shifts are the same for each of the $n+1$ subspectra within the experimental error.

This model is identical to one of those used to successfully interpret the spectra of ^{121}Sb in several Sb-substituted nickel ferrites in previous investigations.[11,23] Seven parameters were varied to obtain a fit of seven pure magnetic hyperfine ^{121}Sb spectra, for Lorentzian-shaped lines in the thin-absorber limit, to the data obtained in the present investigation. These were $H(0)$, y, one isomer-shift parameter, one linewidth parameter for all of the different component lines in all of the different subspectra, an absorption intensity parameter, and two parameters for the parabolic background. The values of the pertinent fitted parameters are given in Table I. y is known from diffraction and magnetization studies to be approximately 0.1.[27] The agreement between the results of the present investigation and those obtained previously[23] is quite good, confirming the validity of the model used to interpret the spectra obtained in zero external field.

The spectra obtained in the 50-kG external field were interpreted in the same manner as the zero-field spectra. However, those absorption lines corresponding to $\Delta m = 0$ were assigned zero intensity in each of the subspectra. In the presence of an external field, Eq. (1) becomes

$$H_{eff}(n) = H_{eff}(0)\frac{1}{6}(6-n) \pm H_{ext}, \quad (3)$$

where the positive sign applies if H_{ext} is parallel to H_{eff} and the negative sign applies if H_{ext} is antiparallel to H_{eff}. The parameters resulting from fitting the applied field spectra are given in Table I. Since $H_{eff}(0)$ is reduced to 220 kG when H_{ext} is 50 kG, H_{eff} at ^{121}Sb must be negative. The decrease of 89 kG in $H_{eff}(0)$ is somewhat larger than the expected decrease of 50 kG, which is certainly due in part to the opposite polarizations in the source and absorber and the subsequent changes in the line positions and intensities.

DISCUSSION

To our knowledge this is the first instance in which the sign of the magnetic hyperfine field at a ^{121}Sb nucleus has been determined using Mössbauer spectroscopy. In spite of the complications arising from the polarization of the source, the spectrum in Fig. 1 should be useful to other Mössbauer investigations of the sign of the magnetic hyperfine field at ^{121}Sb, especially since it will not be pos-

TABLE I. ^{121}Sb Mössbauer parameters of $Ni_{1.2}Fe_{2.7}Sb_{0.1}O_4$ at 100 K.

Sample	H_{ext} (kG)	$H_{eff}(0)$ (kG)	Isomer shift[a] (mm/sec)	y	Linewidth[b] (mm/sec)
$Ni_{1.2}Fe_{2.7}Sb_{0.1}O_4$	0	311 ± 4	-0.401 ± 0.1	0.07	2.4
	50	222 ± 5	-0.401 ± 0.1	0.07	2.4

[a]With respect to $BaSnO_3$ source.
[b]Full width at half-maximum.
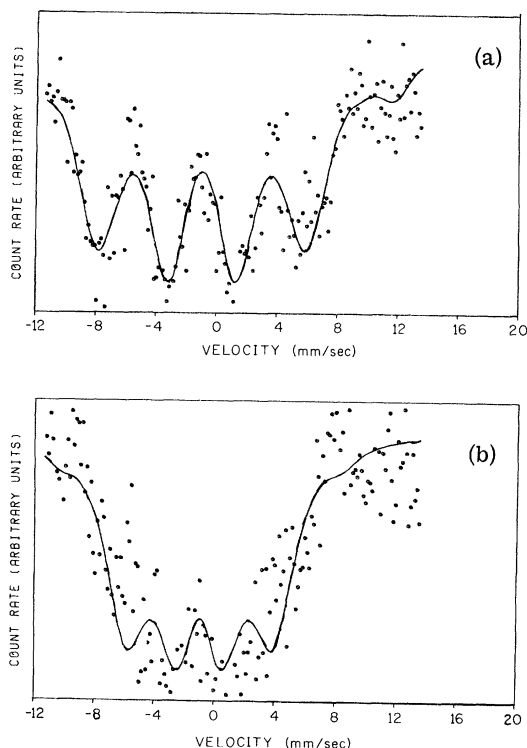
FIG. 1. Mössbauer absorption spectra for $Ni_{1.2}Fe_{2.7}Sb_{0.1}O_4$ between ± 8 mm/sec at 100 K in (a) zero external magnetic field and in (b) a 50-kG external magnetic field applied parallel to the direction of γ-ray propagation.

sible in most cases to obtain spectra in which the source is completely outside the fringing fields of the solenoid at the source strengths currently available.

In accounting for the transferred and supertransferred hyperfine fields, covalence and overlap between the half-filled nd orbitals of the transition-element ion and the filled orbitals of the ligands have been emphasized in theoretical studies. Covalence and overlap involving the nominally unoccupied $(n + 1)s$ orbital have, for the most part, been neglected. Recently, though, Rimmer[28] has considered the effect of covalent mixing a $(n + 1)s$ orbital, using a configuration interaction formalism. Huang et al.[9] have also considered the effect of covalent mixing involving the $4s$ orbital of Mn^{2+} in $KMnF_3$ and MnO using a molecular-orbital approach. In each of these two cases, the total contribution (which involves some cross terms) of the polarized $4s$ electron amounted to more than 50% of the total STHF. However, most of this was due to the polarization of the core s orbitals, and the direct contact contribution of the polarized $4s$ electrons only accounted for about 20% of the total STHF at Mn^{2+} in $KMnF_3$ and MnO. There are still some

questions as to the correctness of these conclusions regarding the relative importance of core polarization by the $4s$ electrons and the direct contact contribution of the $4s$ electrons. Depending upon the value chosen for the difference in the energy of the two configurations A and B listed as follows:

$$\text{configuration } A : \quad Mn^{2+} - O^{2-} - Mn^{2+},$$
$$\text{configuration } B : \quad Mn^{1+} - O^{2-} - Mn^{3+}, \tag{4}$$

the value of the transferred charge in the $4s$ orbital, which is represented by the transfer parameter a given by[9]

$$a^2 = \left(\frac{\langle A | \mathcal{H} | B \rangle - \langle A | B \rangle \langle A | \mathcal{H} | A \rangle}{E_A - E_B} \right)^2 , \tag{5}$$

can be, within the range of possible values of $E_A - E_B$, as much as 2.5 times as large as the value estimated by Huang et al.[9] The sign and magnitude of $E_A - E_B$ dominate the variation in a for the isoelectronic ions, as clearly demonstrated[9] for Mn^{2+} and Fe^{3+}. The numerator in Eq. (5) can be expanded to give (using the notation of Ref. 9)

$$\langle A | \mathcal{H} | B \rangle - \langle A | B \rangle \langle A | \mathcal{H} | A \rangle = (\mathcal{H}_I^{AB} - T'\mathcal{H}_I^{AA})$$
$$- (\mathcal{H}_{13}^{AB} + S_p S_p' \mathcal{H}_I^{AA}) - (\mathcal{H}_{53}^{AB} - S_s S_s' \mathcal{H}_I^{AA}). \tag{6}$$

For $KMnF_3$ and MnO, it has been shown[9] that the last two terms involving the cation-anion transfer tend to be nearly equal and of opposite sign, and thus nearly cancel. The first term $\mathcal{H}_I^{AB} - T'\mathcal{H}_I^{AA}$ represents direct cation-anion d-s transfer. The cation-cation transfer is determined to a very large extent by $E_A - E_B$, increasing with decreasing $E_A - E_B$. The relative behavior of $\mathcal{H}_I^{AB} - T''\mathcal{H}_I^{AA}$ and $E_A - E_B$ makes it possible to base a qualitative discussion of the variations in a for Sb^{5+} and Sn^{4+} on the changes in $E_A - E_B$ alone. A similar strategy has already been used for Mn^{2+} and Fe^{3+}, and the conclusions are qualitatively similar to those arrived at in the present study.

In the present investigation, it is possible to account for the magnitude of the hyperfine field at ^{121}Sb by considering the covalent charge transfer of polarized electrons into the $5s$ orbital and the contact field at the nucleus that would be produced by this charge density, ignoring the polarization of core s orbitals. This is partly justified by the fact that charge transfer into the $5s$ orbital of Sb^{5+} is expected to be considerably greater, and the overlap of the $5s$ orbital with the core s orbitals is expected to be much less than in the case of the $4s$ orbital in $3d$ elements.[29] Ignoring lattice polarization and electron-hole interaction energies, the energy difference $E_A - E_B$ for the two configurations A and B listed below:

$$\text{configuration } A: \quad Fe^{3+} - O^{2-} - Sb^{5+},$$
$$\text{configuration } B: \quad Fe^{4+} - O^{2-} - Sb^{4+}, \tag{7}$$

which correspond to a $3d$-$5s$ transfer, is small, of the order of -1 eV, compared with the 19 eV for Mn^{3+}–Mn^{3+} $3d$-$4s$ transfer and 30 eV for Fe^{3+} – Fe^{3+} $3d$-$4s$ transfer.[30] We therefore expect the STHF to be considerably greater for Sb^{5+} in $NiFe_2O_4$ than for Fe^{3+} and Mn^{2+} in similar materials, as we have observed.

There are at least six mechanisms for transferring spin density to the Sb^{5+} ion.[10] (i) The first, to which we have already alluded, involves the transfer of spin density from the t_{2g} $3d$ orbital of the A-site Fe^{3+} ions to the $5s$ orbital of the Sb^{5+} ion via the covalence of the Fe^{3+}-O^{2-} and Sb^{5+}-O^{2-} linkages. It is known that the covalence of the Fe^{3+}-O^{2-} bond at the A site in spinel ferrites is significantly greater than that at the octahedral B sites[10,24,26]; this coupled with the expected large covalence (electron transfer) of the Sb^{5+}-O^{2-} bond gives this mechanism considerable importance, certainly much more than in the case of octahedral Mn^{2+} ions in MnO and $KMnF_3$. (ii) A second mechanism would involve the overlap of the polarized $2s$ and $2p$ electrons of the oxygen ion with the core s orbitals, e.g., $4s$, $3s$, $2s$, and $1s$. (iii) A third mechanism would be the overlap of the $3d$ orbitals on the Fe^{3+} A-site ions with the $4d$ and core s orbitals. Overlap involving nnn cations have been neglected in theoretical studies because of the large distances involved.[9,28,31,32] In view of the relatively good agreement in some cases and the overestimation in other cases of the STHF in theoretical studies in which these nnn interactions have been neglected, the polarization of core orbitals resulting from nnn overlap must be negligibly small. This third mechanism for STHF will not be considered further. (iv) A fourth mechanism would arise from the finite amplitudes of the $3d$ orbitals of the A-site Fe^{3+} ions and the spin-polarized $2s$ and $2p$ orbitals of the O^{2-} ion at the nucleus of Sb^{5+}. The resultant spin density would then give rise to a magnetic hyperfine field. Huang et al.[9] have argued that the $3d$ orbitals of Mn^{2+} and the $2s$ and $2p$ orbitals of the oxygen have negligible amplitudes at the nucleus of a nnn and nn Mn^{2+} ion, respectively. The $Fe(A)$–O–$Sb(B)$ distance is only about 10% smaller than the Mn—O—Mn distance in MnO, and can be neglected with as much justification in the former case as in the latter.[9,27] (v) A fifth mechanism would involve the overlap of the spin-polarized ligand orbitals with the $4d$ orbitals of the Sb^{5+} ion. This mechanism cannot be of prime importance because a hyperfine field produced mainly by polarized $4d$ electrons would lead to a positive sign for the hyperfine field, in disagreement with the observed negative sign. In addition, this mechanism is inadequate to explain the variations in the hyperfine fields at Sb^{5+} and Sn^{4+} since the overlap of the ligand orbitals with the $4d$ orbitals is greater for Sn^{4+}, yet Sn^{4+} has

the smaller hyperfine field.[29] (vi) A sixth and final mechanism would involve the transfer of $4d$ electrons from the Sb^{5+} ion onto the O^{2-} ion. Since there is a fractional $2p$ hole on the oxygen ion whose spin is antiparallel (called spin down) to that of the local metal moment, there will be a preferential transfer of a spin-down electron from Sb^{5+} to O^{2-}, leaving excess spin-up (parallel to the spin density on the ligand and magnetic cation) spin density in the $4d$ orbital of the antimony ion. This mechanism is very unlikely since the energy difference $E_A - E_B$ between the two configurations A and B, given as follows, is quite large, being approximately 78 eV for the gaseous ions[30]:

$$\text{configuration } A: \quad Sb^{5+}-O^{2-}-Fe^{3+} \ ,$$
$$\text{configuration } B: \quad Sb^{6+}-O^{2-}-Fe^{2+} \ . \tag{8}$$
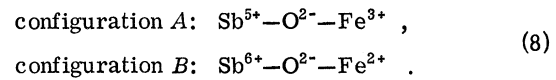
Therefore, of the six possible mechanisms considered above, only the first and second ones, involving $3d$-$5s$ transfer and overlap polarization of core orbitals, are capable of accounting for the STHF at Sb^{5+} in $NiFe_2O_4$.

From a study of the microstatistics of the multiplicity of Sb^{5+} hyperfine fields, it has been established that the transferred spin density comes mainly from the A-site Fe^{3+} ions. It is known that covalence and overlap of the ligand orbitals with a $3d^5$ ion leads to a transferred spin density on the ligand that has the same direction as the local metal moment.[10] The polarized ligand electrons are then transferred via the covalence of the Sb-O bond into the $5s$ orbital of the Sb^{5+} ion. In this mechanism the $5s$ spin moment on the antimony ion therefore has the same direction as the local moment of the A-site Fe^{3+} ion. In an applied magnetic field the A-site moment is antiparallel to the direction of the external field at saturation. The direct contact field of a polarized $5s$ electron is positive, and therefore the magnetic hyperfine field at Sb^{5+} is expected to be antiparallel to the external field (or negative, as observed) if the dominant $3d$-$5s$ transfer is between the A-site Fe^{3+} ions and the Sb^{5+} ions. The agreement between the predicted and the observed negative signs supports the above model when we limit our consideration to the direct Fermi contact interaction of the $5s$ electrons. The overlap polarization of the core s orbital would also lead to a negative sign for the magnetic hyperfine field.

To lowest order, i.e., ignoring mechanisms (iii)–(v) listed above, the STHF originating from the first and second mechanisms is given by[9]

$$\Delta H_{\text{hyp}} \cong \frac{8}{3} \pi g B_e M_s \left(-\sum_{n=1}^{4} \mu_{ns} \phi_{ns}(0) + a\phi_{5s}(0) \right). \tag{9}$$

The core terms, such as $\mu_{ns}^2 \phi_{ns}^2(0)$, have been shown to be important for Mn^{2+}. The contribution

of each of these terms to the STHF has the same
sign as the direct contribution from the 5s elec-
tron. For Mn^{2+} in $KMnF_3$, these core terms make
the major contribution to the STHF, approximately
83% of the net field. However, with increasing
covalence, e.g., in going from $KMnF_3$ to MnO,
the contribution from the core terms decreases
significantly relative to the direct contribution of
the 4s electrons. For $KMnF_3$, ΔH_{hyp} (core)/ΔH_{hyp}
(4s) is about 5, and for MnO this same quantity has
a value of less than 3. We therefore expect the
direct contribution of the polarized 5s electrons in
Sb^{5+} to be at least equal to, and possibly greater
than, the core contributions. Even if the covalence
of the Sb^{5+}-O^{2-} bond is no greater than that of the
Mn^{2+}-O^{2-} bond, which is unlikely, the difference in
$E_A - E_B$ for the configurations listed in Eqs. (4) and
(7) is expected to lead to an a value for Sb^{5+} in
$NiFe_2O_4$ an order of magnitude greater than that
for Mn^{2+} in MnO. While the individual contribu-
tions of cross terms in Eq. (9), such as $\mu_{ns}\phi_{ns}a\,\phi_{4s}$,
are substantial, their sum is quite small and de-
creases rapidly with increasing covalency, being
about 10% of the net hyperfine field for $KMnF_3$
and only 5% of the net field for MnO. Similar ef-
fects are expected for the case of Sb^{5+} and the con-
tribution from the cross terms is therefore believed
to be negligible. For Sb^{5+} it is not possible to esti-
mate unambiguously the relative contributions of
the core s orbitals and the 5s orbital, since no
theoretical estimates are available and such calcu-
lations are outside the scope of the present study.
However, comparing the Mössbauer data for [121]Sb
in $NiFe_2O_4$ with that of [119]Sn in YIG, the contribu-
tions of the core s orbitals are not important in ac-
counting for the *difference* in STHF's at the isoelec-
tronic Sb^{5+} and Sn^{4+} ions having a high degree of
covalence. The observed differences in the mag-
nitudes of the STHF's can be accounted for entirely
on the basis of the difference in the 3d-5s transfer
parameter a.

Before considering the relationship of the results
obtained by Lyubutin for [119]Sn in YIG [12] to the pres-
ent [121]Sb results, we note that the mechanisms
considered above for the STHF at [121]Sb are equally
applicable to the case in which the spin density is
transferred from a B-site Fe^{3+} ion. This possibili-
ty has not been given serious consideration for
$NiFe_2O_4$: Sb for three reasons. First of all, the
multiplicity of the hyperfine fields at [121]Sb could be
accounted for solely on the basis of the presumed
A-B spin transfer. [13,26] In addition, the microsta-
tistics of the [121]Sb hyperfine fields are inconsistent
with a substantial B-B spin transfer. [13,26] Second,
with very few exceptions, the B-B superexchange
interactions are characteristically weak. Since
the strength of the superexchange interaction is
also related to the spin-transfer processes, the

contribution of B-B spin transfer to the STHF at
[121]Sb is also expected to be negligible. [33] Third,
because of the 90° angle between nn B-site ions,
different orbitals of the oxygen ion are involved
in overlap and covalent interactions at the sites
of neighboring B-site ions. It is therefore diffi-
cult to determine the sign of the transferred hyper-
fine field; the theoretical studies on d^3 ions, e.g.,
V^{2+}, are not applicable. [34] On the basis of the pres-
ent data, though, we cannot be absolutely certain
that the contribution of B-B overlap and covalent
spin transfer to the STHF is small. The only ex-
perimental evidence bearing directly on this point,
i.e., the multiplicity of H_{eff} at [121]Sb, is consistent
with the B-B contribution being either constant and
substantial or small over the range of Ni and Fe B-
site occupancies obtainable in Sb-substituted nickel
ferrite. It is definitely established that the A-B
interactions are neither constant nor small over
the composition range studied. Studies on other
Sb-substituted ferrites are being conducted to gain
further insight into the likelihood of these two pos-
sibilities for the B-B interactions.

Returning to the question of the relative impor-
tance of overlap polarization of core ns orbitals
and the covalent spin transfer into the empty 5s
orbital, we note that the mechanisms for the super-
transferred hyperfine interactions proposed by us
for Sb^{5+} are equally applicable to isoelectronic Sn^{4+}
in YIG. The radial extents of the ns core orbitals
of Sn^{4+} are, however, larger than those of Sb^{5+}.
Therefore, if overlap was as important as the cova-
lent spin/charge transfer into the 5s orbital, the
hyperfine field at Sn^{4+} should be larger than, or at
least equal to, that at Sb^{5+}. The magnetic hyper-
fine field at Sb^{5+} is 300 kG and at Sn^{4+} it is only
200 kG, [11] and overlap involving ns core orbitals
cannot be as important as covalent charge/spin
transfer in determining the relative magnitudes of
the hyperfine fields at Sb^{5+} in $NiFe_2O_4$ and Sn^{4+} in
YIG. The cause of this difference in the magni-
tudes of the hyperfine fields cannot be ascribed to
differences in the magnetic environment of the two
ions since the nn anion and nnn cation environments
are virtually identical for an octahedral ion in the
garnet and spinel structures. The nnnn environ-
ments are not similar for an octahedral ion in these
two structure types, [33] but the constancy of the
magnitude of the hyperfine field at [119]Sn in a num-
ber of different rare-earth iron garnets proves
that the nnnn ions have little influence on the hyper-
fine fields. [34] The difference in the magnitudes of
the hyperfine fields at Sn^{4+} and Sb^{5+} is therefore
not due to overlap; since the difference is quite
large, we believe that this result also indicates
that overlap is relatively unimportant on an abso-
lute basis. The difference in the magnitudes of
the hyperfine fields at Sn^{4+} and Sb^{5+} must there-

fore arise from differences in local bonding properties involving the $5s$ orbital.

The $3d$-$5s$ transfer parameter is very sensitive[9] to the energy difference between the configurations A and B. For Sb^{5+}, neglecting the electron-hole interaction and polarization energies, $E_A - E_B$ was estimated to be about -1 eV for the configurations listed in Eq. (7). For Sn^{4+}, the energy difference $E_A - E_B$ for the $3d$-$5s$ transfer, given as follows, is approximately 14 eV[30]:

$$\text{configuration } A: \quad Fe^{3+} - O^{2-} - Sn^{4+},$$

$$\text{configuration } B: \quad Fe^{4+} - O^{2-} - Sn^{3+}. \tag{10}$$

We therefore expect the $3d$-$5s$ charge transfer and the resulting contribution to the contact field to be much greater in Sb^{5+} than in Sn^{4+}.

If the STHF is due entirely to the $5s$ electron, the magnetic hyperfine field is given by the relationship[35]

$$H_{hyp} = (A_{5s} I / \mu_n) \langle S_z \rangle, \tag{11}$$

where the hyperfine coupling constant for a $5s$ electron is given by

$$A_{5s} = \tfrac{16}{3} \pi g_n \mu_N \mu_B | \psi_{5s}(0) |^2 \tag{12}$$

[g_n is the nuclear g factor, μ_B and μ_N are the Bohr and nuclear magnetons, $|\psi_{5s}(0)|^2$ is the density of the $5s$ electrons at the nucleus, I is the nuclear spin, μ_n is the nuclear magnetic moment, and $\langle S_z \rangle$ is the expectation value of the electronic spin of the ion]. Of course, we do not have a full $5s$ electron on either Sb^{5+} in $NiFe_2O_4$ or Sn^{4+} in YIG. The amount of $5s$ charge density is given in each case by the square of the $3d$-$5s$ charge transfer parameter a. Combining Eqs. (10) and (11), and including the parameter a, we obtain the following equation for the hyperfine field on atom i:

$$H_{hyp}^i = (\tfrac{16}{3} \pi \mu_B) \langle S_z \rangle_i \, a_i^2 | \psi_{5s}(0) |_i^2. \tag{13}$$

At this stage we are only interested in the relative magnitudes of the fields at the Sn^{4+} and Sb^{5+} ion, and it is therefore convenient to consider the ratio $H_{hyp}(Sb)/H_{hyp}(Sn)$, i.e.,

$$H_{hyp}^{Sb} / H_{hyp}^{Sn} = [\langle S_z \rangle a^2 | \psi_{5s}(0) |^2]_{Sb} / [\langle S_z \rangle a^2 | \psi_{5s}(0) |^2]_{Sn}. \tag{14}$$

The following simplifications are justified. $\langle S_z \rangle_{Sb}/\langle S_z \rangle_{Sn}$ is very close to unity since this parameter is effectively a measure of the degree of spin polarization of the transferred charge and is determined by the magnetic environment. Since the relevant magnetic environments of Sb^{5+} in $NiFe_2O_4$ and Sn^{4+} in YIG are virtually identical in all respects, e.g., internuclear separations, angles, spin moments, number of magnetic neighbors, etc., the degrees of polarization are expected to be identical and $\langle S_z \rangle_{Sb}/\langle S_z \rangle_{Sn}$ is expected to be equal to one.

$|\psi_{5s}(0)|_{Sb}^2$ and $|\psi_{5s}(0)|_{Sn}^2$ have been calculated for the free ions using nonrelativistic Hartree-Fock wave functions.[21] The ratio $|\psi_{5s}(0)|_{Sb}^2/|\psi_{5s}(0)|_{Sn}^2$ of these calculated values for the free ions is 1.30. Now, due to the orthogonalization of the $5s$ orbital to ligand and metal orbitals, the values of $|\psi_{5s}(0)|_i^2$, i = Sb, and Sn are expected to be somewhat decreased in the solid state. In addition, the relative decrease is expected to be greater for the larger Sn^{4+} ion than for Sb^{5+}, and the value of 1.30 is an upper limit for $|\psi_{5s}(0)|_{Sb}^2/|\psi_{5s}(0)|_{Sn}^2$; the actual value might therefore be closer to unity. The ratio for the free atoms is 1.13.[36] If the transfer parameters were equal to each other for Sn^{4+} and Sb^{5+}, we would obtain

$$H_{hyp}^{Sb}/H_{hyp}^{Sn} = | \psi_{5s}(0) |_{Sb}^2/| \psi_{5s}(0) |_{Sn}^2 = 1.3. \tag{15}$$

The experimental value is 1.5 and the difference in hyperfine fields cannot be due entirely to what is effectively a difference in hyperfine coupling constants.

Suppose, on the other hand, that $|\psi_{5s}(0)|^2$ is approximately the same for Sn^{4+} and Sb^{5+} in the two materials under consideration. Then the following relationship is obtained for $H_{hyp}^{Sb}/H_{hyp}^{Sn}$:

$$H_{hyp}^{Sb}/H_{hyp}^{Sn} \approx a_{Sb}^2 / a_{Sn}^2. \tag{16}$$

Ruby and co-workers[37] have determined the isomer shifts as a function of atomic configuration for several charge states of Sn and Sb. Since the quadrupole splittings are zero within the small experimental errors for both YIG: Sn^{4+} and $NiFe_2O_4$: Sb^{5+}, it is reasonable to neglect configurations involving p electrons. We are therefore left with the configuration $4d^{10}5p^05s^x$. Using the correlation diagrams of Ruby et al.[37] for isomer shift versus electron configuration and the experimentally determined isomer shifts for Sb in $NiFe_2O_4$[13] and Sn in YIG,[11] we obtain x values of 0.16 and 0.1, respectively. It is interesting to note that these values are in qualitative agreement with our conclusions concerning the $3d$-$5s$ transfer in Eqs. (7) and (10). On this basis we therefore expect $H_{hyp}^{Sb}/H_{hyp}^{Sn}$ to be given by

$$\frac{H_{hyp}^{Sb}}{H_{hyp}^{Sn}} = \frac{a_{Sb}^2}{a_{Sn}^2} = \frac{x_{Sb}}{x_{Sn}} = \frac{0.16}{0.1} = 1.6, \tag{17}$$

where x_i is the value of x for atom i in the configuration $4d^{10}5p^05s^x$. The agreement between the above value of 1.6 and the experimental value of 1.5 is quite good.

The good agreement between the experimental value of $H_{hyp}^{Sb}/H_{hyp}^{Sn}$ and the value estimated by assuming the net hyperfine fields to be determined solely by the contact interaction of the $5s$ electrons suggests that there might be a fortuitous cancellation

of the different core terms. We can obtain a quali-
tative confirmation of the likelihood of this hypothe-
sis by considering the degree of polarization of the
x 5s electrons required to produce the observed
fields. For a single fully polarized 5s electron,
the nuclear hyperfine field, including the concomi-
tant core polarization, is estimated to be between
7×10^3 and 15×10^3 kG.[36] For 0.1 and 0.16 of a fully
polarized 5s electron, appropriate to Sn^{4+} in YIG
and Sb^{5+} in $NiFe_2O_4$,[37] respectively, the hyperfine
field is expected to be about 700–1500 kG and 1000–
2400 kG, respectively. To explain the magnitudes
of the observed hyperfine fields, a polarization of
about 20% is expected in each instance. Now we
expect the degree of polarization of the 5s electrons
to be rather similar to that of the sum of the polar-
izations of the oxygen 2s and 2p electrons. For MnO
and CoO, the degrees of polarization of the 2s elec-
trons are found experimentally to be 0.76% and
0.66%, respectively.[38] No experimental value is
available for the polarization of the 2p electrons.
Theoretically, the degree of 2p polarization has
been estimated to be 0.32%.[38] In this same study
the estimate for the 2s polarization was off by a
factor of 3 and if we assume the 2p polarization
estimate to be off by the same factor, we obtain a
maximum value of about 2% for the sum of the 2s
and 2p polarizations. This degree of spin polariza-
tion is only half of that required to produce the ob-
served hyperfine fields at Sb^{5+} and Sn^{4+}. Therefore,
core polarization must be taken into account in
order to explain the absolute magnitudes of the mag-
netic hyperfine fields at Sb^{5+} in $NiFe_2O_4$ and Sn^{4+} in
YIG.

CONCLUSION

The sign and magnitude of the hyperfine field at
the antimony nucleus in Sb-substituted $NiFeO_4$ has
been measured. It is possible to account for both
the sign and magnitude of this hyperfine field as
due primarily to the contact interaction of the po-
larized charge covalently transferred into the 5s
orbital of the Sb^{5+} cation. Overlap of the ligand
orbitals with the 4d orbitals of the Sb^{5+} ion can be
ruled out as an important mechanism because
it would lead to a sign for the hyperfine field oppo-
site to that observed. Upon comparing with results
obtained for Sn^{4+} in YIG, good agreement between
the experimental value of $H_{hyp}^{Sb}/H_{hyp}^{Sn}$ and that esti-
mated assuming the hyperfine field to arise wholly
from the contact interaction of the 5s electrons was
obtained. The experimental values of the hyperfine
fields are probably determined by some complex
interplay between the differences in hyperfine cou-
pling constants and the 3d-5s change transfer param-
eter a. The contribution of the 3d-5s transfer mech-
anism to the STHF is, however, of considerable
importance and appears to be equal to, if not greater
than, any of the other possible mechanisms for
supertransferred hyperfine interactions, at least
for Sb^{5+} in $NiFe_2O_4$ and Sn^{4+} in YIG.

ACKNOWLEDGMENTS

*Academic summer employee, National Bureau of
Standards, Washington, D. C.

[1]J. Owen and J. H. M. Thornley, Rept. Progr. Phys.
24, 675 (1966).

[2]R. G. Shulman and S. Sugano, Phys. Rev. 130, 506
(1963).

[3]K. Knox, R. G. Shulman, and S. Sugano, Phys. Rev.
130, 512 (1963).

[4]J. C. M. Henning, Phys. Letters 24A, 40 (1966).

[5]J. W. Richardson, D. M. Vaught, T. F. Soules, and
R. R. Powell, J. Chem. Phys. 50, 3633 (1969).

[6]A. J. Freeman and R. E. Watson, Phys. Rev. Let-
ters 6, 343 (1961).

[7]S. Nagai, J. Phys. Soc. Japan 25, 510 (1968).

[8]N. L. Huang, R. Ohrbach, and E. Simanek, Phys.
Rev. Letters 17, 134 (1966).

[9]N. L. Huang, R. Ohrbach, E. Simanek, J. Owen,
and D. R. Taylor, Phys. Rev. 156, 383 (1967).

[10]R. E. Watson and A. J. Freeman, in Hyperfine Inter-
actions, edited by A. J. Freeman and R. B. Frankel
(Academic, New York, 1967), p. 90.

[11]V. I. Gol'danskii, M. N. Levisheva, E. F. Makarov,
G. V. Novikov, and V. A. Trukhtanov, Zh. Eksperim.
i Teor. Fiz. Pis'ma v Redaktsiya 2, 63 (1966) [Sov. Phys.
JETP Letters 4, 42 (1966)].

[12]K. P. Belov and I. S. Lyubutin, Zh. Eksperim. i
Teor. Fiz. 49, 747 (1966) [Sov. Phys. JETP 22, 518
(1966)].

[13]S. L. Ruby, B. J. Evans, and S. S. Hafner, Solid
State Commun. 6, 277 (1968).

[14]G. Blasse, in Proceedings of the International Con-
ference on Magnetism, Nottingham, 1964 (Institute of
Physics and The Physical Society, London, 1964), p. 350.

[15]S. Geller, H. J. Williams, G. P. Espinosa, and R.
C. Sherwood, Bell System Tech. J. 43, 565 (1964).

[16]S. Geller, H. J. Williams, G. P. Espinosa, and R.
C. Sherwood, J. Appl. Phys. 35, 542 (1964).

[17]R. L. Streever and G. A. Uriano, Phys. Rev. 139,
A305 (1965).

[18]J. M. Mays, Phys. Rev. 131, 38 (1963).

[19]K. Miyatani, K. Kohn, H. Kamimura, and S. Iida,
J. Phys. Soc. Japan 21, 464 (1966).

[20]G. Matsumoto and S. Iida, J. Phys. Soc. Japan 21,
2734 (1966).

[21]S. L. Ruby and G. M. Kalvius, Phys. Rev. 155, 42
(1967).

[22]J. M. Williams, J. Phys. C 2, 2037 (1969).

[23]S. L. Ruby, in Mössbauer Effect Methodology, edited
by I. J. Gruverman (Plenum, New York, 1967), Vol. 3,
p. 203.

[24]B. J. Evans, Ph.D. thesis (University of Chicago, 1968) (unpublished).

[25]L. J. Swartzendruber, NBS Tech. Note 463 (U. S. GPO, Washington, D. C., 1968).

[26]B. J. Evans, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1968), Vol. 4, p. 139.

[27]G. Blasse, Philips Res. Repts. Suppl. 3, 1 (1969).

[28]D. E. Rimmer, in *Proceedings of the International Conference on Magnetism, Nottingham*, 1964 (Institute of Physics and The Physical Society, London, 1964), p. 337.

[29]C. K. Jorgensen, *Oxidation States and Oxidation Numbers* (Springer-Verlag, Berlin, 1969).

[30]*Atomic Energy Levels*, edited by C. E. Moore, NBS Circ. No. 467 (U.S. GPO, Washington, D.C., 1952).

[31]J. Owen and D. R. Taylor, J. Appl. Phys. 39, 791 (1968).

[32]J. J. Davies, J. Phys. C 1, 849 (1968).

[33]N. L. Huang, Phys. Rev. 157, 378 (1967); D. T. Edmonds and D. R. Taylor, Proc. Phys. Soc. (London) 91, 356 (1967); J. J. Davies and K. Horai, J. Phys. C 4, 682 (1971).

[34]I. S. Lyubutin, Fiz. Tverd. Tela 8, 643 (1966) [Sov. Phys. Solid State 8, 519 (1966)].

[35]W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. 139, A1338 (1965).

[36]L. H. Bennett, R. E. Watson, and G. C. Carter, J. Res. Natl. Bur. Std. (U. S.) 74A, 569 (1970).

[37]S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. 159, 239 (1967).

[38]D. E. O'Reilly and T. Tsang, J. Chem. Phys. 40, 734 (1964).

Dynamical Properties of the Spherical Model in the Low-Temperature and Critical Regions

J. M. J. van Leeuwen

Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, The Netherlands

and

J. D. Gunton[*]

Physics Department, Temple University, Philadelphia, Pennsylvania 19122

(Received 18 June 1971)

The properties of the time-dependent spin correlation functions are investigated for the spherical model of the classical magnetic system. Equations for the correlation functions are derived by a diagrammatic analysis. The lowest-order approximation is for $T > T_c$ identical to the equation derived by Resibois and De Leener for the Weiss limit of the Heisenberg model. Attention has been given to the hydrodynamic regime along the line of spontaneous magnetization from $T = 0$ up to $T = T_c$, where spin-wave frequencies and damping rates as well as the "diffusive" behavior have been calculated to lowest order in the wave number. The dynamical scaling problem is examined within this diagrammatic analysis. The scaling properties and the equations determining the homogeneous correlation function are established explicitly.

I. INTRODUCTION

In this paper we undertake an investigation of the dynamical properties of the spherical model of a classical ferromagnet, both in its critical region and along its coexistence curve. Although the spherical model is not a realistic model for known magnetic systems, there are still several features which make its theoretical study worthwhile. To begin with, the dynamical properties of the classical model of magnetism are intrinsically interesting theoretically, and a spherical version of the model provides a "simple" and nontrivial example of dynamical critical phenomena. Secondly, the behavior of *all* the equal-time multispin correlation functions is known exactly for this model, even in the critical region, as opposed to the situation for more realistic systems. Thus any error involved in computing the transport coefficients would come only from the approximations introduced to handle the dynamical equations, as opposed to the general case where one must also make approximations for the equal-time multispin correlation functions whose validity is often hard to assess. Thirdly, the fact that the dynamics is classical makes it much easier to develop a general diagrammatic analysis for the time-dependent spin-spin correlation function than in the corresponding quantum-mechanical case. On the other hand one has not lost too much physics through these simplifying features of the spherical model, since the equations for the time-dependent spin correlation functions are in lowest order still the same as the equations which follow from Kawasaki's mode-mode coupling theory[1] under much more general circumstances and those obtained by Resibois and De Leener[2] for the Weiss limit of the Heisenberg model for $T > T_c$.