

buildup in the  ${}^4F_{3/2}$  level, it is the inversion relative to a  ${}^4I_{11/2}$  terminal level versus the Yb<sup>3+</sup>  ${}^2F_{5/2}$ - ${}^2F_{7/2}$  inversion which governs the laser threshold. Since the former provides a four-level laser scheme at ambient temperatures whereas the latter provides only a quasi-four-level laser scheme even at 77°K, stimulated emission from Nd<sup>3+</sup> will normally have the lower threshold. Some frequency selective element would therefore be required in

the optical resonator to introduce higher losses at the Nd<sup>3+</sup> laser wavelengths and effectively discriminate against Nd<sup>3+</sup> oscillation.

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## Hyperfine Magnetic Fields at Fe<sup>57</sup> Nuclei in Ferrimagnetic Spinels\*

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The dependence of hyperfine fields at 0°K at Fe<sup>57</sup> nuclei in octahedral (*B*) and tetrahedral (*A*) sites in ferrites on the kind of nearest neighbors is discussed in terms of supertransferred hyperfine fields  $H_{S\text{THF}}$ . An expression for  $H_{S\text{THF}}$  involving the various covalency parameters is derived using the linear combination-of-atomic-orbitals (LCAO) method. From experimental results and the derived expression for  $H_{S\text{THF}}$ , the various covalency parameters are determined for Fe<sup>3+</sup> ions in both *A* and *B* sites. It is found that the Fe<sup>3+</sup>(*A*)-O<sup>2-</sup> bond is considerably more covalent than the Fe<sup>3+</sup>(*B*)-O<sup>2-</sup> bond and that the transfer of O<sup>2-</sup> 2*p* electrons into Fe<sup>3+</sup> 4*s* orbitals is proportional to the transfer into Fe<sup>3+</sup> 3*d* orbitals. We have also found that the hyperfine fields in the various ferrimagnetic spinels can be explained to a large extent by considering only the changes in  $H_{S\text{THF}}$ .

The interesting magnetic properties of ferrimagnetic spinels and garnets originate mainly from the magnetic interactions between cations with magnetic moments which are situated in tetrahedral (*A*) and

octahedral (*B*) sites. The hyperfine fields at Fe<sup>57</sup> nuclei in *A* and *B* sites differ sufficiently for a detailed study with the Mössbauer-effect technique. As we have shown recently,<sup>1</sup> *B*-site nuclei with dif-

ferent distributions of two kinds of cations in the neighboring  $A$  sites experience different hyperfine fields. For example, Mössbauer spectra of not completely inverse spinels show asymmetric broadening of the  $B$ -site lines. Such an asymmetric line consists of several satellite peaks which we have attributed to  $B$ -site iron ions surrounded by different distributions of two kinds of cations in the  $A$  sites. The temperature dependences of the hyperfine magnetic fields at the  $\text{Fe}^{57}$  nuclei in the various  $B$  sites and the  $A$  sites in  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  have been discussed in our previous paper. We also found that at  $0^\circ\text{K}$  the absolute value of the hyperfine magnetic field  $|H_{\text{hpf}}(B)|$  at a  $B$ -site  $\text{Fe}^{57}$  nucleus decreased by  $10 \pm 2$  and  $6 \pm 2$  kOe for every  $\text{Fe}$   $A$ -site nearest neighbor that is replaced by a  $\text{Co}$  or  $\text{Mn}$  ion, respectively. A similar behavior is also found with NMR<sup>2</sup> at  $\text{Fe}^{57}$  nuclei in  $\text{Zn}_x\text{Fe}_2\text{Ni}_{1-x}\text{O}_4$  and with NMR<sup>3</sup> and the Mössbauer-effect technique (ME)<sup>4</sup> at  $\text{Fe}^{57}$  nuclei in diamagnetically substituted garnets.

For a discussion of  $H_{\text{hpf}}(0^\circ\text{K})$ , it is convenient to write the hyperfine field in the following general form:

$$H_{\text{hpf}} = H_c + H_{\text{dip}} + H_{\text{zs}} + H_{\text{cov}}, \quad (1)$$

where  $H_c$  is defined as the contact field at the  $\text{Fe}^{57}$  nucleus for a free ion with  $S_z = \frac{5}{2}$ . So  $H_c$  will be a constant throughout the discussion.  $H_{\text{dip}}$  is the dipolar field produced by the surrounding magnetic ions. This field will change if one of these ions is replaced by an ion with a different magnetic moment. In  $\text{MnFe}_2\text{O}_4$ , however,  $H_{\text{dip}}$  does not change if an iron  $A$ -site or  $B$ -site ion is replaced by manganese because these ions have approximately the same magnetic moments. In other ferites as in  $\text{CoFe}_2\text{O}_4$ ,  $H_{\text{dip}}$  will depend on the distribution of the cations in  $A$  and  $B$  sites. Since the  $A$ -site ions are symmetrically located around a central  $B$ -site iron, the average change in  $H_{\text{dip}}$  will be zero. This effect can cause broadening and may partially explain the relatively broad components of the  $B$ -site line.  $H_{\text{zs}}$  is the change in the hyperfine field in an antiferromagnet due to zero-point spin-wave deviations. The replacement of an antiferromagnetically coupled neighbor by a diamagnetic ion will decrease the spin reduction and consequently also  $H_{\text{zs}}$ .<sup>5</sup> This means that this effect, which is very small, will produce changes of just the opposite sign from those observed. The neighboring anions and cations distort the electronic wave functions and thus the spin distributions of a central cation.  $H'_{\text{cov}}$  gives the change in the hyperfine magnetic field caused by these covalency effects. It is now convenient to write

$$H'_{\text{cov}} = H_{\text{STHF}} + H_{\text{cov}}, \quad (2)$$

where  $H_{\text{STHF}}$  is the supertransferred hyperfine field at a central cation produced by the magnetic moments of nearest-neighbor cations.  $H_{\text{cov}}$  depends

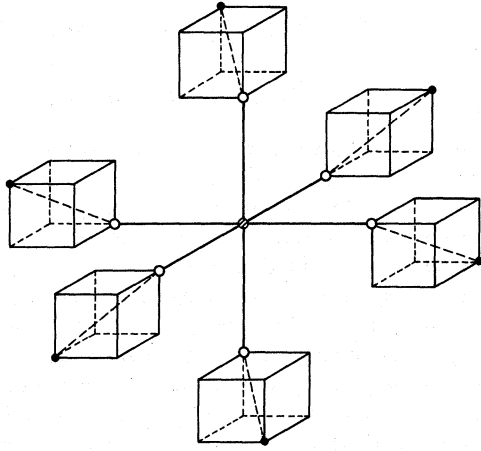
on overlap and transfer from the neighboring anions. Recently, Owen and Taylor<sup>6</sup> and Huang, Orbach, and Simanek<sup>7</sup> have shown that the spin transfer from one metal ion via the ligand to another metal ion can produce contributions to  $H_{\text{hpf}}$  of the order of 10 kOe. The direction of  $H_{\text{STHF}}(B)$  is parallel to  $M_s(A)$  and thus parallel to  $H_c(B)$  if the magnetic moments of the ions  $A$  and  $B$  are antiferromagnetically coupled. For  $\text{Fe}$  ions in  $\text{LaFeO}_3$ , Simanek *et al.*<sup>8</sup> calculated a large value of  $H_{\text{STHF}} = -55$  kOe. A direct observation of  $H_{\text{STHF}} = 210$  kOe at  $\text{Sn}^{119}$  nuclei in the material  $\text{Ca}_x\text{Y}_{3-x}(\text{Fe}_3)\text{Fe}_{2-x}\text{Sn}_x\text{O}_{12}$  has been reported by Belov *et al.*<sup>9</sup> and Goldanskii *et al.*<sup>10</sup> More recently, Evans *et al.*<sup>11</sup> have found  $H_{\text{STHF}} = 300$  kOe at  $\text{Sb}^{121}$  nuclei in  $\text{Sb}$ -substituted ferrites. Streever and Uriano have found  $H_{\text{STHF}} \approx 20$  kOe at  $\text{Ga}$  nuclei in gallium-substituted garnets.<sup>3</sup> Goldanskii *et al.* have shown that the direction of the hyperfine field at  $\text{Sn}^{119}$  nuclei in  $B$  sites is parallel to the magnetic moment of the  $A$ -site ions.<sup>12</sup> Since  $H_{\text{STHF}}$  is also dependent on the kind of nearest-neighbor cations, it probably can explain the experimental results in  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  at  $0^\circ\text{K}$ .

The supertransferred hyperfine field is caused by the overlap distortions of the central ( $B$ ) cation  $s$  orbitals by the ligand orbitals which have been unpaired by transfer into unoccupied  $3d$  orbitals of the neighboring ( $A$ ) cations. The expressions to be derived for  $H_{\text{STHF}}$  here are different from those obtained by Simanek *et al.*<sup>8</sup> in that the  $\text{Fe}(B)$ - $\text{O}$ - $\text{Fe}(A)$  bond angle is  $126^\circ$ , and the transfer into the iron  $4s$  orbitals has been taken into account. The inclusion of the  $4s$  orbitals results in normalization constants for the molecular orbitals which are much smaller than 1, so that the approximations made in Ref. 8 are no longer valid.

To obtain  $H_{\text{STHF}}(B)$  we consider a central  $B$ -site ion surrounded by six oxygen ions each of which has an  $A$ -site nearest neighbor as shown in Fig. 1. In order to obtain the correct normalization constants it is important to treat the problem in this way rather than considering only the  $\text{Fe}(B)$ - $\text{O}$ - $\text{Fe}(A)$  bond and multiplying this result by the number of such bonds. The problem then is to orthogonalize the  $B$ -site  $ns$  orbitals to the ligand orbitals which will have some unpaired spin density because of transfer to unoccupied  $A$ -site iron  $3d$  orbitals. Taking the  $z$  axis to lie along the  $\text{Fe}(B)$ - $\text{O}$  direction, the linear combination of ligand  $p$  orbitals which can combine with the  $\text{Fe}(B)$   $ns$  orbitals is

$$\psi_1^{z'} = 6^{-1/2} [p_{z_1}^{z'} + p_{z_2}^{z'} + p_{z_3}^{z'} + p_{z_4}^{z'} + p_{z_5}^{z'} + p_{z_6}^{z'}].$$

An electron in such an orbital can transfer into an orbital made up of the sum of the six surrounding  $A$ -site  $3d$  orbitals. Taking now the  $\text{Fe}(A)$ - $\text{O}$  direction as the  $z'$  direction and considering only  $\sigma$ -type binding, the proper combination of  $\text{Fe}(A)$   $3d$  orbitals



- oxygen ions
- A-site iron ion
- ⊙ B-site iron ion

FIG. 1. Central B-site iron ion in a spinel structure surrounded by the six nearest oxygen ions and the six nearest A-site iron ions.

is

$$\psi_2^{i,1} = 6^{-1/2} \sum_{i=1}^6 d_{3z_i^2}^{i,1} 2_{-r,2}.$$

The molecular orbitals orthogonalized to the Fe(B)  $ns$  orbitals are

$$\chi^1 = N^1 \left[ \psi_1^1 - \sum_{n=1}^3 S'_{ns} \phi_{ns}^1 + a'_{4s} \phi_{4s}^1 + \gamma \psi_2^1 \right],$$

$$\chi^1 = N^1 \left[ \psi_1^1 - \sum_{n=1}^3 S'_{ns} \phi_{ns}^1 + a'_{4s} \phi_{4s}^1 - S \psi_2^1 \right],$$

where

$$N^1 = \left[ 1 - \sum_{n=1}^3 S_{ns}^2 + a_{4s}^2 + 2a'_{4s} S'_{4s} + \gamma^2 + 2\gamma S \right]^{-1/2}$$

and

$$N^1 = \left[ 1 - \sum_{n=1}^3 S_{ns}^2 + a_{4s}^2 + 2a'_{4s} S'_{4s} - S^2 \right]^{-1/2}.$$

$\phi_{ns}$  and  $\phi_{4s}$  are the B-site  $s$  orbitals, and

$$S_{ns}^{i,1} = \sqrt{6} S_{ns}^{i,1} = \sqrt{6} \langle p_{z'}^{i,1} | \phi_{ns}^{i,1} \rangle,$$

$$a'_{4s}^{i,1} = \sqrt{6} a'_{4s}^{i,1} = \sqrt{6} \times (\text{transfer integral } p_{z'} \rightarrow \phi_{4s}),$$

$$S = \langle p_{z'} | d_{0z'} 2_{-r,2} \rangle = \langle p_{z'} | d_{3z'} 2_{-r,2} \rangle \cos \theta = S_\sigma \cos \theta.$$

$\gamma$  is the transfer integral  $p_{z'} \rightarrow d_{3z'} 2_{-r,2}$  or with  $\gamma = B_\sigma \cos \theta$ , and  $B_\sigma$  is the  $p_{z'} \rightarrow d_{3z'} 2_{-r,2}$  transfer integral. We have taken the B-site spin up and the A-site spin down;  $\pi$  bonding with the A-site ions and

overlap and transfer involving  $O^{2-}$   $1s$  and  $2s$  electrons have been neglected.

The supertransferred hyperfine field is mainly a result of different values for the normalization constants  $N^1$  and  $N^1$ . If we take  $S'_{ns} = S'_{ns} = S'_{ns}$  and  $a'_{4s} = a'_{4s} = a'_{4s}$  and similarly for the  $ns$  orbitals  $\phi_{ns}^1 = \phi_{ns}^1 = \phi_{ns}$ , we find that the net change in spin density at the Fe(B) nucleus is given by

$$|\chi^1(0)|^2 - |\chi^1(0)|^2 \approx 6 [N'^2 - N^2] \times \left[ -\sum_{n=1}^3 S'_{ns} \phi_{ns}(0) + a'_{4s} \phi_{4s}(0) \right]^2.$$

Using the expressions for  $N^1$  and  $N^1$ , we get

$$H_{\text{STHF}}(B) = -525 \times \frac{6}{3} A_\sigma^2(A) N^4 \times \left[ -\sum_{n=1}^3 S'_{ns} \phi_{ns}(0) + a'_{4s} \phi_{4s}(0) \right]^2, \quad (3)$$

where  $A_\sigma^2(A) = [B_\sigma(A) + S_\sigma(A)]^2$ . From here on we will use the notation (A) and (B) as referring to parameters corresponding to ions in A and B sites, respectively. If we now take  $N^1 = N^1 = N$ , that is, neglecting  $B_\sigma$  and  $S_\sigma$  in  $N$  in expression (3), we get

$$N^2 \approx \left[ 1 - 6 \sum_{n=1}^3 S_{ns}^2 + 6a_{4s}^2 + 12a'_{4s} S'_{4s} \right]^{-1}. \quad (4)$$

For the  $H_{\text{STHF}}(A)$ , the central ion is an A-site-iron ion surrounded by four oxygen ions. The  $z$  axis now lies along the Fe(A)-O direction. The linear combination of ligand  $p$  orbitals that can combine with the Fe(A)  $ns$  orbitals is

$$\psi_1^{i,1} = 4^{-1/2} [p_{z_1}^{i,1} + p_{z_2}^{i,1} + p_{z_3}^{i,1} + p_{z_4}^{i,1}].$$

An electron in such an orbital can transfer into an orbital constructed from the 12 surrounding B-site orbitals; each oxygen ion is surrounded by three B-site iron ions. With the Fe(B)-O direction as the  $z'$  direction, the combination of Fe(B)  $3d$  orbitals is

$$\psi_2^{i,1} = 12^{-1/2} \sum_{i=1}^{12} d_{3z_i^2}^{i,1} 2_{-r,2}.$$

The molecular orbitals orthogonalized to the Fe(A)  $ns$  orbitals are

$$\chi^1 = N^1 \left[ \psi_1^1 - \sum_{n=1}^3 S'_{ns} \phi_{ns}^1 + a'_{4s} \phi_{4s}^1 - S \psi_2^1 \right],$$

$$\chi^1 = N^1 \left[ \psi_1^1 - \sum_{n=1}^3 S'_{ns} \phi_{ns}^1 + a'_{4s} \phi_{4s}^1 + \gamma \psi_2^1 \right].$$

Note that the B-site ion has spin up and the A-site ion spin down. Here

$$S_{ns} = \sqrt{4} S'_{ns} = \sqrt{4} \langle p_{z'} | \phi_{ns} \rangle,$$

$$a_{4s} = \sqrt{4} a'_{4s},$$

$$S = \frac{1}{4} [\sqrt{3} S'_\sigma] = \sqrt{3} S'_\sigma,$$

and

$$S'_\sigma = \cos\theta S_\sigma = 3^{-1/2} S_\sigma = 3^{-1/2} \langle p_\pi | d_{3z^2-r^2} \rangle.$$

So,  $S = S_\sigma$  and also  $\gamma = B_\sigma$ . The normalization constants are

$$(N')^2 = \left[ 1 - \sum_{n=1}^3 S_{ns}^{\prime 2} + a_{4s}^{\prime 2} + 2a_{4s}' S_{4s}' - S_\sigma^2 \right]^{-1},$$

$$(N')^2 = \left[ 1 - \sum_{n=1}^3 S_{ns}^{\prime 2} + a_{4s}^{\prime 2} + 2a_{4s}' S_{4s}' + 2B_\sigma S_\sigma + B_\sigma^2 \right]^{-1}.$$

With the same approximation as for  $H_{\text{STHF}}(B)$ , we find that

$$H_{\text{STHF}}(A) = -525 \times 4 A_\sigma^2(B) N^4 \times \left[ - \sum_{n=1}^3 S_{ns}' \phi_{ns}(0) + a_{4s}' \phi_{4s}(0) \right]^2, \quad (5)$$

where

$$N^2 \approx \left[ 1 - 4 \sum_{n=1}^3 S_{ns}^{\prime 2} + 4a_{4s}^{\prime 2} + 8a_{4s}' S_{4s}' \right]^{-1}.$$

The general expression for  $H_{\text{STHF}}(B)$  when more than one kind of  $A$ -site ion is involved, assuming that the contributions of the  $A$ -site ions to  $H_{\text{STHF}}(B)$  are additive, is

$$H_{\text{STHF}}(B) = 525 \times \frac{1}{3} N^4 \left[ - \sum_{n=1}^3 S_{ns}' \phi_{ns}(0) + a_{4s}' \phi_{4s}(0) \right]^2 \times \sum_{i=1}^z C_i A_\sigma^2(A_i), \quad (6)$$

where  $z$  is the number of  $A$ -site nearest neighbors and  $C_i$  is a constant which depends on the number of electrons in the  $3d$  shells. For example,  $C = -1$  for  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Co}^{2+}$  and  $C = 0$  for diamagnetic ions. The supertransferred hyperfine field from the nearest-neighbor  $B$  cations has been neglected, because the  $B$ - $B$  superexchange interaction is usually considerably smaller than the  $A$ - $B$  interaction. For example, the Néel temperature of  $\text{ZnFe}_2\text{O}_4$  was found to be only  $10^\circ\text{K}$ . Superexchange is usually thought of as a transfer from the  $d$  orbital of one ion to the  $d$  orbital of another ion, taking into account the energies involved in such a transfer, while the  $d$  orbital of one ion and the various  $s$  orbitals of the other ion are involved in producing  $H_{\text{STHF}}$  effects. So both effects depend on the spin transfer from one metal ion to another via the ligands, and we expect that  $H_{\text{STHF}}$  and the superexchange will behave, at least qualitatively, in the same way.

For the ferrites discussed in this paper there are only two kinds of  $A$ -site ions, so that

$$H_{\text{STHF}}(B) = 525 \times \frac{1}{3} N^4 \left[ - \sum_{n=1}^3 S_{ns}' \phi_{ns}(0) + a_{4s}' \phi_{4s}(0) \right]^2 \times [IC_1 A_\sigma^2(A_1) + (Z-I)C_2 A_\sigma^2(A_2)], \quad (7)$$

where the subscripts 1 and 2 refer to the two different kinds of  $A$ -site ions and  $I$  is the number of  $A$ -site nearest neighbors of type 1. An additional assumption made in Eqs. (4) and (5) is that  $\langle p | \phi_{ns}^B \rangle$  is independent of the kind of  $A$ -site nearest neighbor. This is not obvious, because an increase in  $\langle p | \phi_{ns}^B \rangle$  is expected with decreasing lattice parameter and, consequently, an increase in  $H_{\text{STHF}}$ . Litster and Benedek have measured the pressure dependence of the hyperfine fields at  $\text{Fe}^{57}$  nuclei in  $A$  and  $B$  sites in yttrium iron garnet (YIG).<sup>13</sup> They found that the hyperfine fields at  $A$ - and  $B$ -site nuclei are nearly independent of the lattice parameters. However, it is possible that other covalency effects cancel at least in part the expected change in  $H_{\text{STHF}}$ . However, in our studies of  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$ , we measure the influence of the kind of  $A$ -site surroundings on the  $B$ -site hyperfine field in the same material. For these cases, we expect that  $\langle p | \phi_{ns}^B(0) \rangle$  is nearly constant.

Equation (7) shows directly how the hyperfine field at a  $B$ -site nucleus depends on the kind of  $A$ -site nearest neighbors. If the  $A$ -site nearest neighbors of type 1 are diamagnetic, then  $C_1 = 0$ , and the decrease in  $|H_{\text{STHF}}|$  and  $|H_{\text{hpf}}|$  is

$$\frac{525}{3} N^4 \left[ - \sum_{n=1}^3 S_{ns}' \phi_{ns}(0) + a_{4s}' \phi_{4s}(0) \right]^2 C_2 A_\sigma^2(A_2) \quad (8)$$

for each ion of type 2 replaced by a diamagnetic ion. In a material with a concentration  $x$  of diamagnetic ions in  $A$  sites, the Mössbauer spectra will, even at  $0^\circ\text{K}$ , be composed of  $6(Z+1)$  lines, with relative intensities of the  $(Z+1)$  spectra given by

$$P(n) = c \binom{6}{n} (1-x)^n x^{6-n}, \quad (9)$$

where  $n$  is the number of diamagnetic nearest neighbors. In NMR studies of  $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$  the average  $B$ -site hyperfine field was found to decrease by 30 kOe at  $77^\circ\text{K}$  in going from  $x=0$  to  $x=0.3$ . Extrapolating this result to  $0^\circ\text{K}$ , we obtain a decrease in  $H_{\text{hpf}}(B)$  of 12 kOe for every  $\text{Fe}$   $A$ -site ion replaced by a  $\text{Zn}$  ion. This yields a field of 483 kOe for  $x=1$  in good agreement with a field of 485 kOe measured in  $\text{ZnFe}_2\text{O}_4$ .<sup>14</sup> The total contribution to  $H_{\text{STHF}}(B)$ , if all the  $A$ -site ions are  $\text{Fe}^{3+}$  ions as in  $\text{NiFe}_2\text{O}_4$ , is then 72 kOe. A decrease in the average hyperfine field at low temperature with increasing diamagnetic substitution has also been observed in  $\text{Ga}_2\text{Fe}_{2-x}\text{M}_x\text{O}_5$ , where  $M$  refers to  $\text{Ga}^{3+}$  or  $\text{Sc}^{3+}$  ions, and also in  $\text{Ga}$ -substituted garnets.<sup>15</sup>

For  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  the situation is slightly

TABLE I. Hyperfine magnetic fields in kOe at an *A*-site iron nucleus, a *B*-site iron nucleus with six nearest-neighbor *A*-site iron ions, and the average field at the *B*-site iron nuclei in various ferrimagnetic spinels.

	$H_{\text{hpf}}(A)$	$H_{\text{hpf}}(B, 6nn \text{ Fe})$	$\langle H_{\text{hpf}}(B) \rangle$
MgFe <sub>2</sub> O <sub>4</sub> (sc)	-500	-537	-530
MgFe <sub>2</sub> O <sub>4</sub> (q)	-509	-540	-525
MnFe <sub>2</sub> O <sub>4</sub>	-512	-550	-520
NiFe <sub>2</sub> O <sub>4</sub>	-515	-555	-555
CoFe <sub>2</sub> O <sub>4</sub> (sc)	-511	-545	-541
CoFe <sub>2</sub> O <sub>4</sub> (q)	-511	-550	-536
Li <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	-518	-545	-545
ZnFe <sub>2</sub> O <sub>4</sub>	...	-557 <sup>a</sup>	-485

<sup>a</sup>Obtained by adding  $H_{\text{STHF}}$  to  $H_{\text{hpf}}(B)$ .

more complicated, because, in addition to the Fe(*A*) ions, also the Co and Mn *A*-site ions will contribute to  $H_{\text{STHF}}(B)$ . In these materials we observe at 0°K a decrease in  $H_{\text{hpf}}(B)$  of  $6 \pm 2$  and  $10 \pm 2$  kOe for every iron *A*-site nearest neighbor replaced by a manganese or a cobalt ion, respectively. The results for MnFe<sub>2</sub>O<sub>4</sub> are the most suitable for a discussion in terms of  $H_{\text{STHF}}$ , because here  $H_{\text{dip}}$  is independent of the distribution in the *A* sites. The average *B*-site hyperfine field of 520 kOe in MnFe<sub>2</sub>O<sub>4</sub> is consistent with a decrease of 6 kOe for every *A*-site iron nearest neighbor replaced by a manganese ion. This can be seen by comparing the measured hyperfine fields in NiFe<sub>2</sub>O<sub>4</sub> (555 kOe) with six iron nearest neighbors in the *A* sites and MnFe<sub>2</sub>O<sub>4</sub> (520 kOe) with on the average 1.2-iron<sup>1</sup> and 4.8-manganese nearest neighbors in the *A* sites. From the results we get  $A_n^2(M_n(A))/A_\sigma^2(\text{Fe}(A)) = \frac{1}{12}(6 \pm 2) \approx 0.5$ , meaning that the spin transfer Mn(*A*) → *L* is half of the spin transfer Fe(*A*) → *L*. This value is in qualitative agreement with the expected relations between supertransfer and superexchange. The value for the ratio of the Mn(*A*)-Fe(*B*) to Fe(*A*)-Fe(*B*) superexchange interaction was found to be 0.66.<sup>1</sup>

From the foregoing discussions it will be clear that the difference in the average hyperfine fields  $\langle H_{\text{hpf}}(B) \rangle$  at a *B*-site iron nucleus can mainly be attributed to the various neighboring *A*-site distributions of two kinds of ions producing different supertransferred hyperfine fields. The hyperfine fields in various ferrites are shown in Table I. The spread in  $\langle H_{\text{hpf}}(B) \rangle$  is rather large, viz., 70 kOe.

It is also interesting to compare the hyperfine fields  $B(\text{Fe } nn)$  at Fe<sup>57</sup> in *B* sites with only iron *A*-site nearest neighbors. For Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, and NiFe<sub>2</sub>O<sub>4</sub> these are directly obtained from measurements, and for MnFe<sub>2</sub>O<sub>4</sub>, MgFe<sub>2</sub>O<sub>4</sub>, and ZnFe<sub>2</sub>O<sub>4</sub> by extrapolating experimental results. The spread in  $H_{\text{hpf}}(B, \text{Fe } nn)$  is about 20 kOe, which may be due to differences in dipolar fields and to differences in lattice parameters which will affect  $H_{\text{cov}}$ .

A similar detailed study as for *B*-site nuclei has not been possible for Fe<sup>57</sup> nuclei in *A* sites. The *A*-site lines certainly show a broadening for example in CoFe<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>, and NiFe<sub>2</sub>O<sub>4</sub> of 0.2 mm/sec and in MgFe<sub>2</sub>O<sub>4</sub> of 0.4 mm/sec corresponding to a distribution in the hyperfine field of 10 and 20 kOe, respectively. The broadening in MgFe<sub>2</sub>O<sub>4</sub> is also temperature dependent. However, the spectra showed no structure in the *A*-site lines and therefore could not be analyzed in order to obtain at 0°K the distribution of hyperfine fields caused by different *B*-site surroundings.

In Table I are also listed the average *A*-site hyperfine fields  $\langle H_{\text{hpf}}(A) \rangle$  in various ferrites. It seems that these fields are not very sensitive to the kind of *B*-site nearest neighbors. However, we can obtain an estimate for  $H_{\text{STHF}}(A)$  from these results. The *A*-site iron in Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub>, MgFe<sub>2</sub>O<sub>4</sub>(q), and MgFe<sub>2</sub>O<sub>4</sub>(sc) have on the average 9, 7, 5, and 6.7 nearest-neighbor iron *B*-site ions, respectively, where *q* indicates quenched and sc slowly cooled. If  $H'_{\text{STHF}}$  is the supertransferred hyperfine field due to one iron *B*-site nearest neighbor, then for *n* neighbors the total transferred field  $H_{\text{STHF}}(A) = nH'_{\text{STHF}}(A)$ . The result is that  $H'_{\text{STHF}}(A) = 8 \pm 3$  kOe; this can be compared with  $H'_{\text{STHF}}(B) \approx 12$  kOe per iron *A*-site nearest neighbor in NiFe<sub>2</sub>O<sub>4</sub>, which has approximately the same lattice parameter as Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub>.

Differences in hyperfine fields in ferrites cannot be explained in detail, because the relative strengths of some of the contributing interactions are not known. We have only considered the Fe(*B*)-Fe(*A*) interaction, which is not always justified. This can be shown by a result obtained by Morel<sup>16</sup> in NiFe<sub>2</sub>O<sub>4</sub>. From the temperature dependences of the magnetization curves, he found that the Ni(*B*)-Fe(*A*) superexchange interaction was also antiferromagnetic and with approximately the same strength

TABLE II. Overlap integrals for the two Fe-O distances in a ferrimagnetic spinel. The symbols used are defined in the text.

Distance	$\Sigma S_{ns}^{+2}$	$\Sigma S_{ns}^{+2}$	$S_\sigma$	$S_{ds}$	$\Sigma S_{ns}^+ \phi_{ns}^+$	$\Sigma S_{ns}^+ \phi_{ns}^+$
Fe( <i>A</i> )-O 1.89 Å	0.015 59	0.015 70	0.071 91	0.302 84	0.708 48	0.703 25
Fe( <i>B</i> )-O 2.03 Å	0.010 195	0.010 267	0.062 36	0.292 76	0.575 55	0.571 67

as the Fe(*B*)-Fe(*A*) superexchange. So not only *B*-site iron ions but also *B*-site nickel ions and probably also *B*-site manganese or copper ions will contribute to the hyperfine magnetic field at an *A*-site iron ion nucleus.

From the experimentally determined supertransferred hyperfine fields  $H_{\text{STHF}}(B) = 72$  kOe for six iron *A*-site nearest neighbors and  $H_{\text{STHF}}(A) = 96$  for 12 iron *B*-site nearest neighbors, we can obtain the "covalency parameters"  $A_o^2(A)$  and  $A_o^2(B)$  from Eqs. (3) and (5). The various overlap integrals  $S_{ns}$  and  $S_o$  and related parameters have been calculated for oxygen-iron distances of 2.03 and 1.89 Å using Watson's spin-polarized Fe<sup>3+</sup> *ns*<sup>17</sup> and oxygen 2*p* wave functions.<sup>18</sup> The  $S_{4s}$  values were obtained using Clementi's iron wave functions<sup>19</sup> for the configurations 3*d*<sup>5</sup>4*s*<sup>2</sup>. The results are given in Table II. Because the transfer integrals  $a_{4s}$  are not known, we have listed in Table III  $A_o^2(A)$  and  $A_o^2(B)$  as determined from Eqs. (3) and (5) for several values of  $a_{4s}^2$ . The occupation of the 4*s* orbitals is given by  $(N^{12} + N^{12})a_{4s}^2$ , so that  $a_{4s}^2(A) = 0.08$  and  $a_{4s}^2(B) = 0.03$  correspond to 4*s* occupations of 0.33 and 0.21 for the *A* and *B* sites, respectively. These are the values suggested by Simanek and Sroubek<sup>20</sup> and result in  $A_o^2(B) = 0.100$  and  $A_o^2(A) = 0.228$ . In Fig. 2 is shown the dependence of  $H_{\text{STHF}}$  on  $a_{4s}^2$  for two different values of  $\phi_{4s}(0)$ , namely, that determined from Clementi's wave functions and that used by Walker *et al.*<sup>21</sup> We notice that  $H_{\text{STHF}}$  for both the *A* and *B* sites does not depend strongly on the 4*s* occupation because of the strong dependence of the normalization constants on  $a_{4s}^2$ . This means that the determination of  $A_o(A)$  and  $A_o(B)$  is not very sensitive to what we take for the 4*s* occupation. So also other processes like the direct 3*d* to 4*s* transfer, which we have neglected, should have a minor influence on the supertransferred hyperfine fields. It should be noted that treating the problem as a cluster of an iron ion plus surrounding oxygen ions results in covalency parameters which are a factor of 2 to 3 larger than from an independent-bond treatment. The reason for this is that the transfer into the unoccupied iron 4*s* orbitals reduces the overlap contribution of 1*s*, 2*s*, and 3*s* orbitals because of the

TABLE III. The spin admixture ( $A_o^2$ ) and the spin transfer ( $B_o^2$ ) parameters for iron ions in *A* and *B* sites for various values of the 4*s* transfer integrals  $a_{4s}^2(B)$  and  $a_{4s}^2(A)$ , respectively.

$a_{4s}^2$	0.00	0.02	0.03	0.04	0.06	0.08	0.10
$A_o^2(A)$	0.195	0.218	0.228	0.239	0.260	0.279	0.298
$B_o^2(A)$	0.137	0.156	0.164	0.174	0.192	0.208	0.225
$A_o^2(B)$	0.088	0.086	0.088	0.090	0.095	0.100	0.105
$B_o^2(B)$	0.055	0.053	0.055	0.056	0.060	0.064	0.068

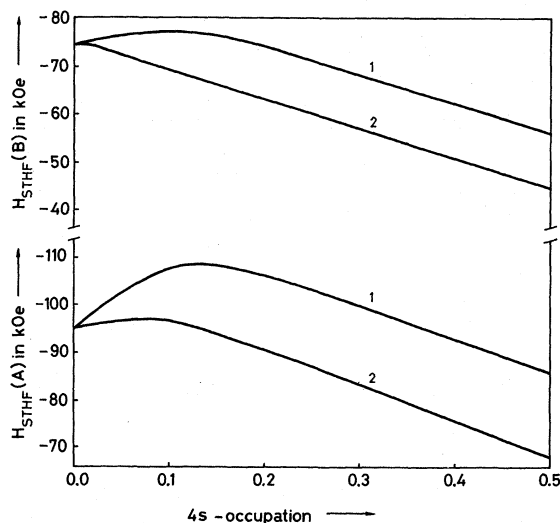


FIG. 2.  $H_{\text{STHF}}(A)$  by 12 nearest *B*-site Fe<sup>3+</sup> ions and  $H_{\text{STHF}}(B)$  by six nearest *A*-site Fe<sup>3+</sup> ions as a function of the 4*s* occupation. 1 and 2 have been calculated using  $\phi_{4s}(0)$  from Refs. 21 and 19, respectively.

removal of oxygen 2*p* electrons of the corresponding symmetry. In the cluster calculation, such as we have done here, there are only two electrons in the correct linear combination of oxygen 2*p* orbitals with nonzero overlap with the central iron *s* wave functions. On the other hand, in the independent-bond model one considers that there are essentially 12 electrons in the oxygen 2*p* orbitals which can combine with the *s* orbitals of iron ions in octahedral sites. These two approaches, therefore, lead to different normalization constants. In expressions (3) and (5) the constant  $N^4 \approx 0.3$ , while in the independent-bond model  $N$  is usually taken to be 1.

From Table III we see that the iron ions in the *A* sites are considerably more covalent than those in the *B* sites. In fact, the transfer of oxygen 2*p* electrons into the empty 3*d* orbitals of Fe(*A*) is three times larger than the transfer of 2*p* electrons into the 3*d* orbitals of Fe(*B*).

In this paper we have shown that the spread in hyperfine fields in *A* and *B* sites in the various ferrites is largely due to different supertransferred hyperfine fields. From the experimentally determined supertransferred hyperfine fields, we have found the parameters  $A_o(A)$  and  $A_o(B)$  which are a measure of the degree of admixture of the 2*p* ligand and 3*d* iron wave functions. The supertransferred hyperfine fields are found to be quite insensitive to the degree of 4*s* occupation. Further, it is interesting to note that the occupations of the 4*s* orbitals for Fe in *A* and *B* sites, as suggested by Simanek and Sroubek, yield a ratio  $a_{4s}^2(A)/a_{4s}^2(B) \approx 2.7$  which

is rather close to the ratio of the transfer into 3d orbitals, namely,  $B_0^2(A)/B_0^2(B) \approx 2.6$ . This is what one would expect qualitatively considering only the Fe-O distances.

In a subsequent publication we will discuss the difference in the A- and B-site hyperfine fields in ferrites and garnets as well as Fe<sup>3+</sup> hyperfine fields measured in other compounds.

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## Parquet Diagrams in the Local-Moment Problem

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Parquet diagrams are used to self-consistently include vertex corrections to the paramagnon propagator in the Suhl model of local-moment formation. The equations are solved numerically in an approximation valid at high temperatures. Curie-law behavior for the self-consistent susceptibility is not found; instead the susceptibility varies roughly as  $T^{-2/3}$ . A conserving approximation to the susceptibility based on the parquet-diagram approximation for the mass operator is also investigated. This gives a susceptibility which diverges at finite  $T$ . Possible consequences of abandoning the high-temperature approximation are discussed.

### I. INTRODUCTION

Suhl<sup>1</sup> has developed a model of local-moment formation based on the Anderson<sup>2</sup> or Wolff<sup>3</sup> models in which the strong intra-atomic Coulomb repulsion between localized  $d$  electrons of opposite spin, broadened by conduction-electron scattering, forms long-lived spin fluctuations in the localized state. The lifetime of the spin fluctuations, or localized paramagnons, is much longer than that of the  $d$

electrons themselves. At high temperatures this leads to a Curie-law susceptibility for the localized state, and at lower temperatures  $\ln T$  behavior of the resistivity, reminiscent of the Kondo effect,<sup>1,4,5</sup> is found, though the Kondo temperature and the Curie constant predicted by this model are much smaller than is expected.<sup>5</sup> The model requires a self-consistent calculation of the  $d$ -electron propagator, renormalized by paramagnon exchange, and the paramagnon propagator, which is essential-