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Cation-Cation Interaction Contributions to the Hyperfine Interaction. The "Supertransferred Hyperfine Interaction"*

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The change in hyperfine field at a central cation site when the nearest-neighbor cation sites are occupied by magnetic ions is calculated. Two mechanisms dominate this effect: one an orthogonalization of the neighboring magnetic ion's σ orbitals to the inner s shells of the central cation; the other a charge transfer process from the neighboring magnetic ion's σ orbitals to the unoccupied s orbitals on the central cation. Specific application is made to Mn^{2+} in two hosts, $KMgF_3$ and MgO. It is shown that the hyperfine field at the Mn^{2+} site *increases* by 10.8 kG and (more approximately) 21.1 kG, respectively, for $KMnF_3$ and MnO, as compared with the values in the dilute salts. This increase, together with the observed nuclear resonance hyperfine-field frequency in the antiferromagnetic state, allows for a reduction in sublattice magnetization, due to zero-point motion, of 3.2% for $KMnF_3$ and 2.5% in MnO, in essential agreement with the predictions of spin-wave theory. A qualitative discussion is given of similar changes in Fe^{3+} salts; and of Cr^{3+} salts where the effect is shown to be of opposite sign.

I. INTRODUCTION

THE change in the hyperfine field at the site of a magnetic ion brought about by the presence of a neighboring magnetic ion was first demonstrated by Heeger and Houston.[1] In two recent letters[2,3] we reported mechanisms for this change and termed it the "supertransferred hyperfine field," (STHF).[4] We considered the linear structure M_2-L-M_1, where M_1 and M_2 are two magnetic ions with antiparallel spins and L is an intervening ligand. One mechanism arises from the unpairing of the spins in the s cores of M_2 via overlap with a polarized σ orbit on the ligand. This ligand polarization, or unpaired spin density, is caused by the transfer of a ligand σ electron from L to M_1. In addition to this mechanism, a $3d$ electron can also be transferred from M_1 to the empty s shells of M_2 via a direct transfer $M_1 \rightarrow M_2$ or via an indirect process in which an electron is transferred from L to M_2 and another simultaneously transferred from M_1 to L. In the antiferromagnetic state the spin of M_1 will be antiparallel to that of M_2, so that the unpaired spin in the s orbitals of M_2 is oppositely directed to the $3d$ spins of M_2. Both mechanisms result in an enhancement of the hyperfine interaction because the $3d$ electrons give rise to a negative spin density at the nucleus (core polarization), whereas the s electrons contribute positively.

A number of investigators have shown[5–7] that $A_c\langle S\rangle$ in the concentrated antiferromagnet is very nearly equal to A_dS measured in the dilute salt. If one supposes that $A_c=A_d$, this implies that $\langle S\rangle$ is very nearly equal to S, in disagreement with antiferromagnetic spin-wave theory[5,8,9] which, because of zero-point motion, argues for a ~3% decrease. An increase in A_c over A_d would, however, allow for a compensating decrease in the sublattice magnetization of a few percent, in much better agreement with the predictions of antiferromagnetic spin-wave theory.

In this paper the change in the hyperfine field upon going from Mn^{2+}:$KMgF_3$ to $KMnF_3$ and Mn^{2+}:MgO to MnO is calculated. The previous estimates in Ref. 3 are improved by taking into account not only the $2p_\sigma$ orbitals of the ligand but also the $2s$ orbitals. Because of the relative signs of the overlap integrals involved in the cation-cation interactions, inclusion of the $2s$ ligand orbitals reduces the previous result[3] for the increase in the hyperfine field A_c over A_d.

In addition, it is interesting to compare Cr^{3+} and Fe^{3+} salts with our results for Mn^{2+}. In the former case, transfer of parallel spin electrons from the σ ligand orbitals to the unoccupied $3d$ and $4s$ orbitals on the Cr^{3+} ion leads to a ligand polarization of opposite sign from that found in $3d^5$ configuration salts. This results in a STHF of opposite sign to that found for Mn^{2+} and Fe^{3+} salts, a result predicted and verified recently by

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[1] A. J. Heeger and T. W. Housten, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and the Physical Society, London, 1964), p. 395.

[2] J. Owen and D. R. Taylor, Phys. Rev. Letters **16**, 1164 (1966).

[3] Nai Li Huang, R. Orbach, and E. Šimánek, Phys. Rev. Letters **17**, 134 (1966).

[4] It should be pointed out that a very similar treatment is contained in the work of H. Kamimura, J. Phys. Soc. Japan **21**, 484 (1966).

[5] M. E. Lines and E. D. Jones, Phys. Rev. **139**, A1313 (1965).

[6] H. Montgomery, D. T. Teaney, and W. M. Walsh, Jr., Phys. Rev. **128**, 80 (1962).

[7] V. Minkiewicz and A. Nakamura, Phys. Rev. **143**, 356 (1966).

[8] R. Kubo, Phys. Rev. **87**, 568 (1952); J. M. Ziman, Proc. Phys. Soc. (London) **A65**, 540 (1952); **A65**, 548 (1952).

[9] H. L. Davis, Phys. Rev. **120**, 789 (1960).

Taylor and Owen.[10] The latter case, that of Fe^{3+} salts, is one where considerable confusion can be said to still exist. The smaller lattice constant and larger covalency found for Fe^{3+} as compared to Mn^{2+} salts would seem to argue for a larger STHF in the former case. This is apparently in disagreement with a number of experiments, and is discussed at some length in Sec. IV of this paper.

II. DERIVATION OF THE CHANGE OF THE HYPERFINE FIELD CAUSED BY CATION-CATION INTERACTIONS

In this section we construct an antibonding molecular orbital which describes the covalent mixing of the ligand orbitals into the d orbitals at $Mn^{2+}(1)$ and includes the charge transfer from the d orbitals at $Mn^{2+}(1)$ to the $4s$ orbital at $Mn^{2+}(2)$. The atomic orbitals involved are shown in Fig. 1. The resulting molecular orbital should be orthogonal not only to the bonding orbitals at the ligand but also to the s cores at $Mn^{2+}(2)$ site. The latter, being orthogonalized to the bonding orbitals at the ligand, take the following form to lowest order [we neglect the overlap integrals between the s cores at $Mn^{2+}(2)$ and $3d$ orbitals at $Mn^{2+}(1)$]:

$$\psi_{ns}(2)=N_2[\phi_{ns}+S_{p,ns}(p_z+B_\sigma d_z^2)-S_{s,ns}(s+B_s d_z^2)],\qquad(1)$$

where

$$S_{p,ns}=-\langle p_z|\phi_{ns}\rangle,\quad S_{s,ns}=\langle s|\phi_{ns}\rangle,\qquad(2)$$

and $p_z+B_\sigma d_z^2$ and $s+B_s d_z^2$ are the bonding orbitals at the ligand transforming like p_z and s orbitals, respectively. Therefore, the antibonding molecular orbital at $Mn^{2+}(1)$ can be written as

$$\psi_{z^2}(1)=N_1\left[d_{z^2}-A_\sigma p_z-A_s s-\sum_{n=1}^{3}\mu_{ns}\psi_{ns}(2)+a\phi_{4s}\right],\qquad(3)$$

where A_σ and A_s are the cation-ligand covalent mixing parameters, the coefficient a is the $3d\rightarrow 4s$ charge transfer parameter and μ_{ns} is determined from the required orthogonality between (1) and (3), $\langle\psi_{z^2}(1)|\psi_{ns}(2)\rangle=0$. We find, retaining the dominant terms,

$$\mu_{ns}\simeq A_\sigma S_{p,ns}-A_s S_{s,ns};\quad n=1,2,3.\qquad(4)$$

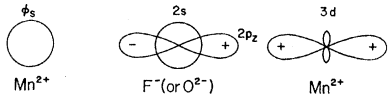

FIG. 1. Atomic orbitals involved in constructing the antibonding molecular orbital given by Eq. (3) in the text.

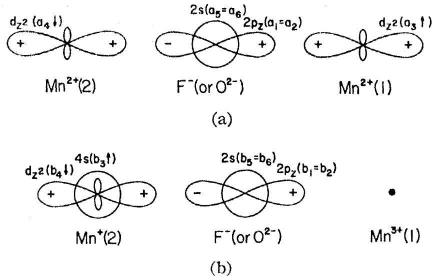

FIG. 2. (a) Orbitals considered in the ionic configuration A; (b) Orbitals considered in the excited configuration B where an electron is transferred from the d_z^2 orbital of $Mn^{2+}(1)$ to the $4s$ orbital of $Mn^{2+}(2)$.

The change in the hyperfine field at the nucleus of $Mn^{2+}(2)$ caused by the presence of the $Mn^{2+}(1)$ ion, is given by

$$\Delta H_{\text{hyp}}=(8\pi/3)g\beta_e M_s|\psi_{z^2}(0)|^2,\qquad(5)$$

where ψ_{z^2} is given by (3). Since the $2s$ and $2p$ orbitals of the ligand and the $3d_{z^2}$ orbital of $Mn^{2+}(1)$ ion have negligible amplitudes at the site of $Mn^{2+}(2)$ ion, we can approximate (5) to lowest order by

$$\Delta H_{\text{hyp}}\simeq(8\pi/3)g\beta_e M_s\left[-\sum_{n=1}^{3}\mu_{ns}\phi_{ns}(0)+a\phi_{4s}(0)\right]^2.\qquad(6)$$

The square of the $3d\rightarrow 4s$ transfer parameter a in (3) denotes the amount of charge that is transferred from the d_{z^2} orbital of $Mn^{2+}(1)$ to the $4s$ orbital of the neighboring $Mn^{2+}(2)$ ion. Higher unoccupied s orbitals are neglected because their energies are much higher than that of the $4s$ level; and, moreover, because the hyperfine field reduces by roughly an order of magnitude in going from an ns level to a higher $(n+1)s$ level. We determine the cation-cation $3d\rightarrow 4s$ charge transfer parameter a in the following way. Consider the ground configuration A, shown in Fig. 2(a); and the excited configuration B, shown in Fig. 2(b); wherein an electron has been transferred from the d_{z^2} orbital of one cation to the unoccupied $4s$ orbital of the neighboring cation. The perturbed ground-state wave function is given by

$$\psi=\psi^A+a\psi^B,\qquad(7)$$

where

$$a=\frac{\langle A|\mathcal{H}|B\rangle-\langle A|B\rangle\langle A|\mathcal{H}|A\rangle}{E_A-E_B}.\qquad(8)$$

The numerator of (8) can be evaluated by using the Dirac-VanVleck-Serber permutation degeneracy method.[11–14] For the case of two antiparallel spins on orbitals a_3 and a_4 (or b_3 and b_4), we can make the

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[10] D. R. Taylor and J. Owen (to be published).

[11] P. A. M. Dirac, *The Principle of Quantum Mechanics* (Clarendon Press, Oxford, England, 1958).

[12] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

[13] R. Serber, Phys. Rev. **45**, 461 (1934).

[14] Nai Li Huang and R. Orbach, Phys. Rev. **154**, 487 (1967).

following expansion:

$$\begin{aligned}\langle A|\mathcal{H}|C\rangle &\\ \simeq \mathcal{H}_I{}^{AC}-\mathcal{H}_{13}{}^{AC}-\mathcal{H}_{14}{}^{AC}+\mathcal{H}_{34}{}^{AC}-\mathcal{H}_{134}{}^{AC}-\mathcal{H}_{143}{}^{AC} &\\ +2\mathcal{H}_{13,24}{}^{AC}-\mathcal{H}_{53}{}^{AC}-\mathcal{H}_{54}{}^{AC}-\mathcal{H}_{534}{}^{AC}-\mathcal{H}_{543}{}^{AC} &\\ +2\mathcal{H}_{53,64}{}^{AC}, &\quad (9)\\ C=A \quad \text{or} \quad B, &\end{aligned}$$

where

$$\mathcal{H}_P{}^{AC}=\langle Pa_1a_2\cdots a_6|\mathcal{H}|c_1c_2\cdots c_6\rangle, \qquad (10)$$
$$c=a \quad \text{or} \quad b.$$

The labeling of the above atomic orbitals is shown in Fig. 2. The order of magnitude of each term in (9) is given very roughly by

$$\mathcal{H}_P{}^{AC}\simeq\mathcal{H}_I{}^{AC}\langle Pa_1a_2\cdots a_6|c_1c_2\cdots c_6\rangle. \qquad (11)$$

We have therefore omitted in (9) terms which involve orthogonal orbitals in the sense of (11). Defining the overlap integrals

$$\begin{aligned} S_p&=\langle a_1|a_3\rangle; & S_p'&=-\langle a_1|b_3\rangle;\\ S_s&=\langle a_5|a_3\rangle; & S_s'&=\langle a_5|b_3\rangle;\\ T&=\langle a_3|a_4\rangle; & T'&=\langle a_3|b_3\rangle; \qquad (12)\end{aligned}$$

and neglecting in (9) terms of order higher than $T'\mathcal{H}_I{}^{AA}$ or $SS'\mathcal{H}_I{}^{AA}$, we obtain the following expression for the parameter a:

$$a=\frac{(\mathcal{H}_I{}^{AB}-T'\mathcal{H}_I{}^{AA})-(\mathcal{H}_{13}{}^{AB}+S_pS_p'\mathcal{H}_I{}^{AA})-(\mathcal{H}_{53}{}^{AB}-S_sS_s'\mathcal{H}_I{}^{AA})}{E_A-E_B}. \qquad (13)$$

III. EVALUATION OF (6), THE CHANGE IN HYPERFINE FIELD DUE TO CATION-CATION INTERACTIONS

In this section we wish to estimate the supertransferred hyperfine field for the cases of KMnF$_3$ and MnO. We adopt the approximation that both materials have perfect cubic symmetry and that the nearest magnetic neighbors in KMnF$_3$ and the next-nearest magnetic neighbors in MnO have antiparallel spin orientations. In MnO, there are six parallel and six antiparallel magnetic near neighbors. The contributions to the supertransferred hyperfine field coming from the nearest neighbors thus cancel in the antiferromagnetic state, and only the next nearest neighbors contribute. We consider these two cases, KMnF$_3$ and MnO, separately.

A. KMnF$_3$

We can calculate the change in the hyperfine field on a Mn^{2+} ion using (4), (6), and (13). The parameters A_σ and A_s are related, respectively, to the $2p$-$3d$ and $2s$-$3d$ covalency parameters by the simple expressions $A_\sigma\simeq\lambda_{2p\text{-}3d}/\sqrt{3}$ and $A_s\simeq\lambda_{2s\text{-}3d}/\sqrt{3}$. Using the experimental values for the spin densities on the F$^-$ ion in KMnF$_3$,[15] $f_\sigma=1.2\%$ and $f_s=0.5\%$, we find $A_\sigma=0.11$ and $A_s=0.07$. The overlap integrals defined in (2) are computed using Watson's free-ion wave functions for the Mn^{2+} ion,[16] and for the F$^-$ ion.[17] They are

$$S_{p,1s}=0.0017;\quad S_{p,2s}=0.0131;\quad S_{p,3s}=0.0684;$$
$$S_{s,1s}=0.0002;\quad S_{s,2s}=0.0019;\quad S_{s,3s}=0.0147. \qquad (14)$$

Substituting these values for A_σ, A_s and the overlap integrals S into (4), we obtain

$$\mu_{1s}=0.00017;\quad \mu_{2s}=0.00131;\quad \mu_{3s}=0.00650. \qquad (15)$$

The estimation of the $3d\rightarrow4s$ charge transfer parameter a is rather involved. Consider the spin-independent Hamiltonian

$$\mathcal{H}=\sum_i-\frac{\hbar^2}{2m}\nabla_i{}^2-\sum_{i,g}\frac{Z_ge^2}{r_{ig}}+\sum_{i>j}\frac{e^2}{r_{ij}}, \qquad (16)$$

where Z_g is the atomic number of the nucleus at the point g. In order to simplify the calculations the ligand $2p$ and $2s$ electrons are treated separately. For each case a four-electron model is adopted where, in the ground state, two electrons with opposite spin occupy a ligand orbital and one d electron is located on each of the two magnetic ions, as in Fig. 2. The excited configuration corresponds to the transfer of a d_σ electron from one magnetic ion to the $4s$ level of the other magnetic ion. Because of the nonorthogonality of the atomic orbitals, this excited configuration contains *both* direct cation-cation and cation-anion, anion-cation transfer processes outlined in the Introduction. Using (10), the first term in the numerator of (13) corresponding to direct cation-cation transfer becomes,

$$\mathcal{H}_I{}^{AB}-T'\mathcal{H}_I{}^{AA}=\langle a_1a_2a_3a_4|\mathcal{H}|b_1b_2b_3b_4\rangle$$
$$-T'\langle a_1a_2a_3a_4|\mathcal{H}|a_1a_2a_3a_4\rangle. \qquad (17)$$

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[15] This value is estimated from the results of neutron scattering measurements in MnF$_2$ (R. Nathans, G. Will, and D. E. Cox, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1964), p. 327, and the NMR measurements in KMnF$_3$ [R. G. Shulman and K. Knox, Phys. Rev. **119**, 94 (1960)]. J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, Proc. Phys. Soc. (London) 88, 13 (1966).

[16] R. E. Watson, MIT SSMTG Technical Report, No. 12, 1959 (unpublished).

[17] R. E. Watson (private communication).

Šimánek and Tachiki[18] point out that because of the high-frequency character of the virtual excitation involved in cation-cation or anion-cation charge transfer, charge redistribution in the excited configuration has no "time" to develop fully during the virtual transfer process. Consequently, the one-electron orbitals b_1, b_2, b_4, b_5, and b_6 in our excited configuration are, to a good approximation, the same as the one-electron orbitals a_1, a_2, a_4, a_5, and a_6 in the ground configuration, respectively. Writing the Hamiltonian as the sum of one-electron operators $\mathcal{H}_i$ and the two-electron operators e^2/r_{ij}, (17) becomes,

$$\begin{aligned}\mathcal{H}_I{}^{AB}-T'\mathcal{H}_I{}^{AA}={}&\langle a_3|\mathcal{H}_1|b_3\rangle-T'\langle a_4|\mathcal{H}_1|a_4\rangle\\&+2\left\langle a_1a_3\middle|\frac{e^2}{r_{ij}}\middle|a_1b_3\right\rangle-2T'\left\langle a_1a_3\middle|\frac{e^2}{r_{ij}}\middle|a_1a_3\right\rangle+\left\langle a_3a_4\middle|\frac{e^2}{r_{ij}}\middle|b_3a_4\right\rangle-T'\left\langle a_3a_4\middle|\frac{e^2}{r_{ij}}\middle|a_3a_4\right\rangle.\end{aligned}\tag{18}$$

Similarly, we find that the anion → cation (2) and simultaneous cation (1) → anion transfer integral involving ligand $2p_\sigma$ orbitals is given by

$$\begin{aligned}\mathcal{H}_{13}{}^{AB}+S_pS_p'\mathcal{H}_I{}^{AA}={}&\langle a_3a_2a_1a_4|\mathcal{H}|b_1b_2b_3b_4\rangle+S_pS_p'\langle a_1a_2a_3a_4|\mathcal{H}|a_1a_2a_3a_4\rangle\\={}&-\langle a_3|\mathcal{H}_1|a_1\rangle S_p'+S_pS_p'\langle a_1|\mathcal{H}_1|a_1\rangle+\langle a_1|\mathcal{H}_1|b_3\rangle S_p+S_pS_p'\langle a_4|\mathcal{H}_1|a_4\rangle\\&-\left\langle a_3a_1\middle|\frac{e^2}{r_{ij}}\middle|a_1a_1\right\rangle S_p'+\left\langle a_3a_1\middle|\frac{e^2}{r_{ij}}\middle|a_1b_3\right\rangle-\left\langle a_3a_4\middle|\frac{e^2}{r_{ij}}\middle|a_1a_4\right\rangle S_p'+\left\langle a_1a_1\middle|\frac{e^2}{r_{ij}}\middle|a_1b_3\right\rangle S\\&+3\left\langle a_1a_4\middle|\frac{e^2}{r_{ij}}\middle|a_1a_4\right\rangle S_pS_p'+\left\langle a_1a_4\middle|\frac{e^2}{r_{ij}}\middle|b_3a_4\right\rangle S_p+\left\langle a_1a_1\middle|\frac{e^2}{r_{ij}}\middle|a_1a_1\right\rangle S_pS_p'+\left\langle a_3a_4\middle|\frac{e^2}{r_{ij}}\middle|a_3a_4\right\rangle S_pS_p'.\end{aligned}\tag{19}$$

The (similar) transfer integral involving the ligand $2s$ orbitals is given by

$$\begin{aligned}\mathcal{H}_{53}{}^{AB}-S_sS_s'\mathcal{H}_I{}^{AA}={}&\langle a_5a_4a_3a_6|\mathcal{H}|b_3b_4b_5b_6\rangle-S_sS_s'\langle a_3a_4a_5a_6|\mathcal{H}|a_3a_4a_5a_6\rangle\\={}&\langle a_3|\mathcal{H}_1|a_5\rangle S_s'-\langle a_5|\mathcal{H}_1|a_5\rangle S_sS_s'+\langle a_5|\mathcal{H}_1|b_3\rangle S_s-\langle a_4|\mathcal{H}_1|a_4\rangle S_sS_s'\\&+\left\langle a_3a_5\middle|\frac{e^2}{r_{ij}}\middle|a_5a_5\right\rangle S_s'+\left\langle a_3a_5\middle|\frac{e^2}{r_{ij}}\middle|a_5b_3\right\rangle+\left\langle a_3a_4\middle|\frac{e^2}{r_{ij}}\middle|a_5a_4\right\rangle S_s'+\left\langle a_5a_5\middle|\frac{e^2}{r_{ij}}\middle|a_5b_3\right\rangle S_s\\&-3\left\langle a_5a_4\middle|\frac{e^2}{r_{ij}}\middle|a_5a_4\right\rangle S_sS_s'+\left\langle a_5a_4\middle|\frac{e^2}{r_{ij}}\middle|b_3a_4\right\rangle S_s-\left\langle a_5a_5\middle|\frac{e^2}{r_{ij}}\middle|a_5a_5\right\rangle S_sS_s'-\left\langle a_3a_4\middle|\frac{e^2}{r_{ij}}\middle|a_3a_4\right\rangle S_sS_s'.\end{aligned}\tag{20}$$

Using the $4s$ wave function for Mn^+ calculated by Rimmer,[19] Watson's functions[16,17] for the Mn^{2+} $3d$ orbitals and the F^- $2p$ orbitals, the one-center and two-center two-electron integrals in (18)–(20) can be accurately evaluated using the modified version of the Switendick-Carbato MIDIAT program.[20] The program is unreliable only for the Coulomb integral between two electrons centered at two nuclei far apart. For this case we use a point charge model. The values of the *two-electron* integrals are listed in Table I for $KMnF_3$.

The effect of the electrons other than those considered in the four-electron model can be approximately taken into account by assuming the following one-electron Hamiltonian to be used in (18)–(20).

$$\mathcal{H}_1=-(\hbar^2/2m)\nabla_1{}^2+V_1(Mn^{3+})+V_2(Mn^{3+})+V(F^+),\tag{21}$$

where $V_1(Mn^{3+})$, $V_2(Mn^{3+})$, and $V(F^+)$ are the effective Hartree one-electron potential energies arising from the Mn^{3+} ion at cation 1 site, the Mn^{3+} ion at cation 2 site and the F^+ ion, respectively. The ionicities have been chosen in the above manner so that the interactions between the four electrons under consideration are not included again in (20).

Evaluation of the matrix elements of (21) in (18)–(20) is carried out in the following manner. Consider $\langle a_3|\mathcal{H}_1|a_1\rangle$ as an example. Using (21) for $\mathcal{H}_1$,

$$\begin{aligned}\langle a_3|\mathcal{H}_1|a_1\rangle={}&\left\langle a_3\middle|\frac{-\hbar^2\nabla^2}{2m}\middle|a_1\right\rangle+\langle a_3|V_1(Mn^{3+})|a_1\rangle\\&+\langle a_3|V_2(Mn^{3+})|a_1\rangle+\langle a_3|V(F^+)|a_1\rangle.\end{aligned}\tag{22}$$

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[18] E. Šimánek and M. Tachiki, Phys. Letters **21**, 625 (1966), and E. Šimánek, Ž. Sroubek, and M. Tachiki, J. Phys. Soc. (Japan) (to be published).

[19] D. E. Rimmer (private communication).

[20] A. C. Switendick and F. J. Corbato, MIT SSMTG, Quarterly Progress Report No. 34, 1959 (unpublished).

TABLE I. The two-electron integrals $\langle\phi_1\phi_2\|\phi_3\phi_4\rangle\equiv\langle\phi_1\phi_2|e^2/r_{ij}\times|\phi_3\phi_4\rangle$ involved in (17), (18), and (19) for $KMnF_3$. The values are given in atomic units.

$\langle a_1a_3\|a_1a_3\rangle=0.2745$
$\langle a_3a_4\|b_3a_4\rangle=0.0019$
$\langle a_3a_4\|a_3a_4\rangle=0.0669$
$\langle a_3a_1\|a_1a_1\rangle=0.0465$
$\langle a_1a_4\|b_3a_4\rangle=-0.0857$
$\langle a_1a_1\|a_1b_3\rangle=-0.0946$
$\langle a_1a_1\|a_1a_1\rangle=0.8135$
$\langle a_3a_5\|a_5a_5\rangle=0.0400$
$\langle a_5a_5\|a_5b_3\rangle=0.1299$
$\langle a_5a_4\|a_5a_4\rangle=0.2609$
$\langle a_5a_5\|a_5a_5\rangle=0.8835$
$\langle a_5a_4\|b_3a_4\rangle=0.0615$
$\langle a_3a_4\|a_1a_4\rangle\simeq0.01$
$\langle a_3a_1\|a_1b_3\rangle\simeq0.004$
$\langle a_3a_4\|a_5a_4\rangle\simeq0.01$
$\langle a_3a_5\|a_5b_3\rangle\simeq0.003$
$\langle a_1a_3\|a_1b_3\rangle$[a]

[a] We are unable to estimate this matrix element, and have ignored it in the computation of a_{4s}.

TABLE II. The one-electron integrals entered in (18), (19), and (20) for $KMnF_3$, in atomic units. Overlap integrals defined in (12) are also listed.

$\langle a_3|\mathcal{H}_1|b_3\rangle=-0.0209$
$\langle a_4|\mathcal{H}_1|a_4\rangle=-1.8317$
$\langle a_3|\mathcal{H}_1|a_1\rangle=-0.2337$
$\langle a_1|\mathcal{H}_1|a_1\rangle=-2.5891$
$\langle a_1|\mathcal{H}_1|b_3\rangle=0.5225$
$\langle a_3|\mathcal{H}_1|a_5\rangle=-0.2208$
$\langle a_5|\mathcal{H}_1|a_5\rangle=-3.4759$
$\langle a_5|\mathcal{H}_1|b_3\rangle=-0.6785$
$S_p=0.0739$
$S_p'=0.2138$
$S_s=0.0606$
$S_s'=0.02004$
$T=0.0011$
$T'=0.0088$

Consider the Hartree equation for the orbital a_1 of the F^- ion,

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(F^+)+e^2\int\frac{a_2^*(2)a_2(2)}{r_{12}}dr_2\right]a_1(1)$$
$$=\epsilon_H(F^-)a_1(1). \quad (23)$$

Similarly, we have

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_1(Mn^{3+})\right]a_3=\epsilon_H(Mn^{2+})a_3. \quad (24)$$

Multiplying (23) by a_3 and (24) by a_1 and integrating over all space, we obtain

$$\langle a_3|\mathcal{H}_1|a_1\rangle=\epsilon_H(F^-)S_p$$
$$-\left\langle a_3a_2\left|\frac{e^2}{r_{12}}\right|a_1a_2\right\rangle+\epsilon_H(Mn^{2+})S_p$$
$$+\left\langle a_1\left|\frac{\hbar^2}{2m}\nabla^2\right|a_3\right\rangle+\langle a_3|V_2(Mn^{3+})|a_1\rangle. \quad (25)$$

We approximate the Hartree energies $\epsilon_H(F^-)$ and $\epsilon_H(Mn^{2+})$ appearing in (25) by the one-electron energies calculated in the Hartree-Fock approximation.[16,21] The remainder of the terms in (25) are evaluated from Table I or by explicit calculation. The same procedure is followed for the remainder of the one-electron integrals, and the results are listed in Table II. We also list in Table II the values of the overlap integrals defined by (12). Using the results presented in Tables I and II, the various contributions to the $3d\rightarrow4s$ transfer, (18), (19), and (20), are, respectively,

$$\mathcal{H}_I^{AB}-T'\mathcal{H}_I^{AA}=-0.008,$$
$$\mathcal{H}_{13}^{AB}+S_pS_p'\mathcal{H}_I^{AA}=0.016,$$
$$\mathcal{H}_{53}^{AB}-S_sS_s'\mathcal{H}_I^{AA}=-0.017. \quad (26)$$

These values show that the contributions coming from the ligand $2p$ and $2s$ orbitals tend to cancel. Physically, this cancellation occurs because the $2p$ orbitals have positive overlap with the cation on the left and negative overlap with the cation on the right, whereas the $2s$ orbitals have positive overlap with both cations. Hence the contributions to the $3d\rightarrow4s$ transfer involving the ligand $2p$ orbitals are of opposite sign. Near cancellation occurs because the $2s$ orbital is more stable than the $2p$ orbital, compensating for the decrease in S_sS_s' as compared with S_pS_p'.

Next, we estimate the energy difference between the ground and the excited configurations. We adopt the measured values[22] for the energy of a $3d$-electron in the $3d^5$ configuration of Mn^{2+} ion and for a $4s$ electron in the $3d^5(\uparrow)4s(\downarrow)$ configuration of the Mn^+ ion. We must also include the electronic polarization correction and the electron-hole interaction energies. We calculate the electric field at the sites of the anions in the immediate vicinity of M_1 and M_2 caused by the extra electron at M_2, the hole at M_1 and the induced electric dipole at the intervening ligand. The polarization energy is estimated by using the static formula $\sum_i \alpha_i E_i^2$ and a reduction factor of roughly 3 because of the high-frequency character of the virtual charge transfer processes, as discussed by Šimánek and Tachiki.[18] We find a polarization energy of 2.2 eV for $KMnF_3$. The electron-hole interaction energy is found to be 1.6 eV.

TABLE III. Contributions to the super transferred hyperfine field (in kilogauss) in $KMnF_3$. Diagonal terms are given by $\Delta H_{ns,ns}=16\pi g\beta_e M s\mu_{ns}^2|\phi_{ns}(0)|^2$ and $\Delta H_{4s,4s}=16\pi g\beta_e M s a^2|\phi_{4s}(0)|^2$. Cross terms are given by $\Delta H_{ns,ms}=32\pi g\beta_e M s\mu_{ns}\mu_{ms}\phi_{ns}(0)\phi_{ms}(0)$ and $\Delta H_{ns,4s}=-32\pi g\beta_e M s\mu_{ns}a\phi_{ns}(0)\phi_{4s}(0)$. Here $n\neq m=1$, 2, and 3.

$\Delta H_{1s,1s}$	$\Delta H_{2s,2s}$	$\Delta H_{3s,3s}$	$\Delta H_{4s,4s}$	$\Delta H_{1s,2s}$	$\Delta H_{1s,3s}$	$\Delta H_{2s,3s}$	$\Delta H_{1s,4s}$	$\Delta H_{2s,4s}$	$\Delta H_{3s,4s}$	ΔH_{hyp}
0.4	2.3	7.7	1.9	−2.0	3.7	−8.5	2.1	−4.2	7.7	10.8

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[21] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).
[22] *Atomic Energy Levels*, edited by C. E. Moore, Nat. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing and Publishing Office, Washington, D. C., 1952).

This value is considerably smaller than that found for anion-cation transfer because of the shielding of the intervening ligand, which we have approximately taken into account by the use of a high-frequency dielectric constant $\epsilon \simeq 2$. The energy denominator for $3d \rightarrow 4s$ transfer is then found to be the sum of the difference in the energy between a $3d$ electron in the $3d^5$ configuration of Mn^{2+} and in the $3d^5(\uparrow)4s(\downarrow)$ configuration of Mn^+, and the previously mentioned corrections. We find, $E_B - E_A = 15.4$ eV. Using this value, and inserting (26) into (13), we obtain for $KMnF_3$[23]

$$a \simeq 1.2 \times 10^{-2}. \qquad (27)$$

We substitute the values for the inner ns shell orthogonalization parameters, μ_{ns}, given by (15), and the value for a found in (27) into (6). We also make use of Watson's wave functions[24] to evaluate the amplitudes of the ns cores at the nucleus and Rimmer's[19] wave function for the amplitude of the $4s$ orbital at the nucleus. We multiply (6) by a factor of 6 to allow for the additive effect of the six Mn^{2+} antiparallel near (magnetic) neighbors in $KMnF_3$. Putting all these factors together, we list in Table III the entirety of the contributions to the super transfer hyperfine field, including both diagonal and cross terms. The total change in the hyperfine field at a Mn^{2+} site upon going from Mn^{2+}:$KMgF_3$ to $KMnF_3$ is found to be 10.8 Kg. Equivalently, the change in the hyperfine constant is 1.52×10^{-4} cm^{-1}. Montgomery *et al.*[6] extrapolate a value of $A = 91.64 \times 10^{-4}$ cm^{-1} for Mn:$KMgF_3$ for a lattice constant appropriate to that of $KMnF_3$. Hence, adding the expected increase in A due to the supertransferred hyperfine interaction, we predict a hyperfine constant of

$$A_{KMnF_3} = 93.16 \times 10^{-4}\ \text{cm}^{-1}, \qquad (28)$$

for Mn^{2+} in concentrated $KMnF_3$. Using the hyperfine frequency of 676 ± 3 M_c/sec for $KMnF_3$ measured by Minkiewicz and Nakamura,[7] we then find a zero-point spin-wave reduction of the sublattice magnetization of

$$1 - \langle S \rangle / S = 3.2\%. \qquad (29)$$

TABLE IV. The values of μ_{ns} defined in (4) for several assumed values of A_σ for MnO.

A_σ	μ_{1s}	μ_{2s}	μ_{3s}
0	−0.00003	−0.00021	−0.00149
0.05	0.00008	0.00059	0.00262
0.11	0.00020	0.00155	0.00755
0.14	0.00026	0.00203	0.01002
0.18	0.00035	0.00267	0.01331

TABLE V. The two-electron integrals involved in (18), (19), and (20) for MnO in atomic units.

$\langle a_1a_3 \| a_1a_3 \rangle = 0.2614$
$\langle a_3a_4 \| b_3a_4 \rangle = 0.0012$
$\langle a_3a_4 \| a_3a_4 \rangle = 0.0631$
$\langle a_3a_1 \| a_1a_1 \rangle = 0.0418$
$\langle a_1a_4 \| b_3a_4 \rangle = 0.1035$
$\langle a_1a_1 \| a_1b_3 \rangle = -0.1037$
$\langle a_1a_1 \| a_1a_1 \rangle = 0.6390$
$\langle a_3a_5 \| a_5a_5 \rangle = 0.0332$
$\langle a_5a_5 \| a_5b_3 \rangle = 0.1193$
$\langle a_5a_4 \| a_5a_4 \rangle = 0.2450$
$\langle a_5a_5 \| a_5a_5 \rangle = 0.7392$
$\langle a_5a_4 \| b_3a_4 \rangle = 0.0644$
$\langle a_3a_4 \| a_1a_4 \rangle \simeq 0.01$
$\langle a_3a_1 \| a_1b_3 \rangle \simeq 0.005$
$\langle a_3a_4 \| a_5a_4 \rangle \simeq 0.009$
$\langle a_3a_5 \| a_5b_3 \rangle \simeq 0.003$
$\langle a_1a_3 \| a_1b_3 \rangle$[a]

[a] We are unable to estimate this matrix element, and have ignored it in the computation of a_{4s}.

B. MnO

In MnO, neutron-diffraction measurements[25] yield the result $f_\sigma + 2f_\pi + f_s = 3.3\%$ for the unpaired spin densities on the $0^=$ ligand. Nuclear-magnetic-resonance experiments on O^{17} in paramagnetic MnO (powder) by O'Reilly and Tsang[26] yield a value of $f_s = 0.76\%$ for the spin density in the oxygen $2s$ orbitals. This leads to a value of $A_s = 0.09$. Because of the lack of additional experimental information giving us a relation between f_σ and f_π, we are unable to obtain a value for f_σ alone. Thus we are unable to compute the parameter A_σ in our antibonding molecular orbital (3). We shall therefore calculate the supertransferred hyperfine interaction for possible values of A_σ varying from zero to 0.18. Very roughly speaking, A_σ is proportional to the overlap integral between the $2p_z$ and $3d_{z^2}$ orbitals. Comparing the values of this overlap integral for $KMnF_3$ and MnO, we find a value of A_σ about 0.11. Watson's

TABLE VI. The one-electron integrals entered in (18), (19), and (20) for MnO, in atomic units. Overlap integrals defined by (12) are also listed.

$\langle a_3 | \mathcal{H}_1 | b_3 \rangle = -0.0130$
$\langle a_4 | \mathcal{H}_1 | a_4 \rangle = -1.5695$
$\langle a_3 | \mathcal{H}_1 | a_1 \rangle = -0.2218$
$\langle a_1 | \mathcal{H}_1 | a_1 \rangle = -2.2472$
$\langle a_1 | \mathcal{H}_1 | b_3 \rangle = 0.6013$
$\langle a_3 | \mathcal{H}_1 | a_5 \rangle = -0.1908$
$\langle a_5 | \mathcal{H}_1 | a_5 \rangle = -2.9553$
$\langle a_5 | \mathcal{H}_1 | b_3 \rangle = -0.5832$
$S_p = 0.0748$
$S_p' = 0.2704$
$S_s = 0.0586$
$S_s' = 0.2148$
$T = 0.0006$
$T' = 0.0060$

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[23] The Šimánek-Tachiki (Ref. 18) reduction of the lattice polarization energy results in a 40% reduction of the transfer coefficient a over its value when the "full" (i.e., static) lattice polarization is allowed to develop. Because of $4s$-ns cross terms, this reduction results in a 40% reduction of the STHF from the value appropriate to a static polarization energy correction. Thus, our results for the magnitude of the STHF are, unfortunately, quite sensitive to the magnitude of the energy denominator appearing in the expression for the transfer coefficient (13).

[24] *Magnetism IIA*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1966), p. 249. Amplitudes of the s-cores at the nucleus site can be calculated from the individual s-electron contributions to the contact hyperfine fields for Mn^{2+} listed in Table XI.

[25] R. Nathans, G. Will, and D. E. Cox, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1964), p. 327.

[26] D. E. O'Reilly and Tung Tsang, J. Chem. Phys. **40**, 734 (1964).

TABLE VII. Contributions to the supertransferred hyperfine field (in kilogauss) in MnO. The notations are defined in Table III.

A_σ	$\Delta H_{1s,1s}$	$\Delta H_{2s,2s}$	$\Delta H_{3s,3s}$	$\Delta H_{4s,4s}$	$\Delta H_{1s,2s}$	$\Delta H_{1s,3s}$	$\Delta H_{2s,3s}$	$\Delta H_{1s,4s}$	$\Delta H_{2s,4s}$	$\Delta H_{3s,4s}$	ΔH_{hyp}
0.00	0.0	0.1	0.4	5.8	−0.0	0.2	−0.3	−0.6	1.2	−3.1	3.7
0.05	0.1	0.5	1.3	5.8	−0.4	0.7	−1.6	1.5	−3.3	5.4	10.0
0.11	0.6	3.3	10.4	5.8	−2.8	5.0	−11.7	3.7	−8.8	15.6	21.1
0.14	1.0	5.6	18.4	5.8	−4.8	8.6	−20.4	4.9	−11.5	20.7	28.3
0.18	1.8	9.8	32.4	5.8	−8.5	15.4	−35.6	6.5	−15.1	27.5	40.0

wave functions for the Mn^{2+} ion[16] and the O^{2-} ion,[27] yield the following values for the overlap integrals between the $O^{=}$ ligand and the *ns* cores of the Mn^{2+} ion,

$$S_{p,1s}=0.0021;\quad S_{p,2s}=0.0160;\quad S_{p,3s}=0.0822;$$
$$S_{s,1s}=0.0003;\quad S_{s,2s}=0.0023;\quad S_{s,3s}=0.0165.$$

The values for μ_{ns} defined by (4) are listed in Table IV for several assumed values of A_σ. The evaluation of the 3*d*-4*s* transfer parameter *a* can be carried out in a manner identical with our method for estimating *a* in $KMnF_3$. The relevant two-electron and one-electron integrals are given in Tables V and VI. We find for MnO,

$$\mathcal{H}_I{}^{AB}-T'\mathcal{H}_I{}^{AA}=-0.007,$$
$$\mathcal{H}_{13}{}^{AB}+S_pS_p'\mathcal{H}_I{}^{AA}=0.022,$$
$$\mathcal{H}_{53}{}^{AB}-S_sS_s'\mathcal{H}_I{}^{AA}=-0.018. \qquad (30)$$

Introducing a polarization energy for MnO of 4.6 eV, found in a manner identical to that for $KMnF_3$, and an electron-hole interaction energy of 0.7 eV appropriate to MnO, we find

$$a\simeq 2.1\times 10^{-2}. \qquad (31)$$

The contributions to the supertransfer hyperfine field are given in Table VII. A parabolic curve is drawn in Fig. 3 to show the behavior of ΔH_{hyp} as a function of the parameter A_σ, keeping the parameter *a* fixed. Using the value of $A=81.55\times 10^{-4}\ \text{cm}^{-1}$ measured by Walsh *et al.*[28] for Mn:MgO, the resulting values of *A* in MnO are listed in Table VIII for various values of A_σ. Using the hyperfine frequency of 617.8 Mc/sec determined by Lines and Jones[5] for MnO, we deduce a 2.5% decrease in the sublattice magnetization for our "best guess" value of $A_\sigma=0.11$. For other values of A_σ the corresponding decreases in $\langle S\rangle/S$ are also given in Table VIII.

TABLE VIII. Estimated values of the hyperfine constant for Mn in MnO and associated changes in sublattice magnetization due to zero-point spin-wave fluctuation, using our Table VII and the results of Ref. 3. The boldface terms are our "best guess" values.

A_σ	A (10^{-4} cm^{-1})	$1-\langle S\rangle/S$ (%)
0.00	82.07	−0.4
0.05	82.96	0.7
0.11	**84.52**	**2.5**
0.14	85.53	3.7
0.18	87.17	5.5

IV. DISCUSSION

We believe we have demonstrated in this paper the important role of cation-cation interaction contributions to the hyperfine interaction. It is clear that our method is easily generalized to similar configurations, for instance the Fe-O-Al complex in Fe^{3+}:$LaAlO_3$ discussed by Taylor and Owen.[10] The inner *ns* shells of the Al^{3+} ion are polarized by the mechanism outlined in Sec. II, leading to a change in the field seen by an Al^{3+} nucleus. In addition, transfer to the unoccupied Al^{3+} 3*s* orbit may also contribute to the super transfer hyperfine interaction on the Al^{3+} site, as it did for Mn^{2+}-L-Mn^{2+} complex. Similar effects have been noted at the Ga^{3+} site in Fe^{3+}:YGaG by Streever and Uriano[29] and by Chen *et al.*[30] for V^{4+} in SnO_2.

It is interesting to consider the supertransfer hyperfine interaction between other pairs of iron group ions. One such system, Fe^{3+}-L-Fe^{3+}, at first appears to be very similar to the cases we have considered in detail in this paper. The covalency parameters are generally much larger[25] for Fe^{3+} than for Mn^{2+} so at first, from (4), one might expect the effect on the hyperfine field of

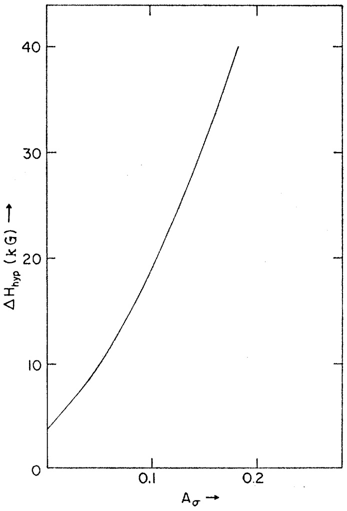

FIG. 3. A plot of the supertransferred hyperfine field as a function of A_σ [defined in Eq. (3) of the text] for MnO.

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[27] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

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

[29] R. L. Streever and G. A. Uriano, Phys. Rev. Letters **12**, 516 (1964); Phys. Rev. **139**, A305 (1965).

[30] I. Chen, C. Kikuchi, and H. Watanabe, J. Chem. Phys. **42**, 186 (1965).

cation-cation interactions to be much larger. Treves[31] quotes the hyperfine fields for Fe^{3+} in $MFeO_3$ compounds, where M is a rare-earth ion, ranging between 545 and 560 kG. Unfortunately, the "dilute" value of the hyperfine field (e.g., Fe^{3+}:$LaAlO_3$) is unknown, though as a rough comparison Locher and Geschwind[32] find hyperfine fields of 547.7 and 548.0 kG for Fe^{3+} in CaO and MgO, respectively.

We can compute a *lower* limit to ΔH_{hyp} for Fe^{3+} in $LaFeO_3$ by using the method described in this paper, but ignoring $4s$ transfer. This neglect may be partially justified by considering the energy for $3d \rightarrow 4s$ transfer between cations. Neglecting the electronic polarization energy we find $\Delta E_{3d\rightarrow 4s}=30$ eV from the atomic energy levels[22] for Fe^{3+}. This is to be compared with 19 eV obtained[3] for the same transfer between two Mn^{2+} ions. Subtraction of the polarization (and the electron-hole) energies suffices to further increase the ratio of transfer energies, thereby reducing the importance of $4s$ transfer for iron salts. A similar reduction has been noted by Rimmer[33] who deduced that the ligand $2p$ or $2s$ transfer to the vacant cation $4s$ orbital is much smaller for Fe^{3+} than for Mn^{2+}. Using the expressions given previously in this paper, we obtain $\Delta H_{\mathrm{hyp}}=51$ kG, or about a 10% increase in the antiferromagnetic state compared to Fe^{3+} in a dilute oxide. Even a spin-wave reduction of $\langle S\rangle$ by 3% leads to a calculated 7% (or 35 kG) increase in the antiferromagnetic state. If we use the Locher and Geschwind results for Fe^{3+}:MgO as a measure of the "dilute" hyperfine field, this magnitude of increase is not found experimentally.

We believe the resolution to this difficulty lies with the O^{2-} wave function.[34] It is well known that O^{2-} does not exist as a free ion and it is further doubted[27] "that a Hartree-Fock solution, which is a simple determinant s.c.f. (self-consistent-field) calculation, would converge to a state with all ten electrons bound for a free O^{2-}." Yamashita and Kojima[35] computed the O^{2-} $2p$ wave function including the potential (and exchange) caused by an octahedron of positive charges surrounding the oxygen ion. Watson[27] solved for the entirety of the 10 orbitals introducing a sphere of positive charge at the ionic radius of the oxygen ion. Both calculations indicated a sensitivity to the magnitude of the superimposed potential.

It is our argument that, for the specific case of $LaFeO_3$, with a Fe^{3+}-O^{2-} distance of 1.945 Å, the oxygen wave functions are considerably different (in fact, smaller) than in, say, MnO, where the Mn^{2+}-O^{2-} distance is 2.22 Å. This occurs because of a decrease in lattice constant, and because of an increase in cation charge. Watson[27] shows the latter effect acts to "sharpen up" the $2p$ radial wave function and to reduce the total ionic energy (including the well energy) from -156.1194 Ry to -163.4968 Ry. Because Watson's $2p$ wave functions for O^{2-} are in fact quite close to Yamashita and Kojima's, and because the latter authors used an octahedron of charges with lattice constant appropriate to MgO, we argue that the Watson's O^{2-} wave functions which we used for $LaFeO_3$ in fact are more appropriate to MnO. The overlaps calculated for $LaFeO_3$ are therefore too large because the oxygen orbitals are inappropriate (too expanded) for $LaFeO_3$.[36] To estimate the magnitude of this effect, we have computed ΔH_{hyp} for a Fe^{3+}-O^{2-} *distance* appropriate to MnO, but with the covalency parameters appropriate to $LaFeO_3$. We find $\Delta H_{\mathrm{hyp}}=23.8$ kG, or a reduction of more than 50% from our estimate using Watson's O^{2-} wave functions and a lattice constant appropriate to $LaFeO_3$. It is interesting to note that this result is in rather good agreement with Treves's result for $LaFeO_3$ if we take the Locher and Geschwind[32] result for Fe^{3+} in MgO (548 kG), add to it the value we calculate for the "scaled" $LaFeO_3$ (+23.8 kG), and subtract 3% from zero-point spin-wave reduction of $\langle S\rangle$ (-17.2 kG). The value we obtain, 555 kG, is very close to Treves's[31] 560 kG result for $LaFeO_3$. The "close" agreement with Treves' result is of course somewhat suspicious and represents only the lower limit for ΔH_{hyp} since we have ignored the $4s$ transfer coefficient a. Nevertheless, it does demonstrate the sensitivity of our results to the precise form of the O^{2-} wave function. It would be of great interest to have the O^{2-} functions for a potential well appropriate to $LaFeO_3$ in order to explicitly test our predictions for the magnitude of the supertransferred hyperfine field in the iron-oxide salts.

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[31] D. Treves, J. Appl. Phys. **36**, 1033 (1965).

[32] P. P. Locher and S. Geschwind, Phys. Rev. **139**, A991 (1965).

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

[34] E. Šimánek, Nai Li Huang, and R. Orbach, J. Appl. Phys. **38**, 1072 (1967).

[35] J. Yamashita and M. Kojima, J. Phys. Soc. Japan **7**, 261 (1952).

[36] As an example, the $O^{2-}(2p)-Fe^{3+}(3s)$ overlap calculated for $LaFeO_3$ equals 0.11, whereas the corresponding quantity for MnO equals 0.08.