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llmCd IN ANTIFERROMAGNETIC NiO, CoO, AND MnO

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SUPERTRANSFERRED HYPERFINE INTERACTION:
PERTURBED ANGULAR CORRELATION OF $^{111m}\text{Cd}$
IN ANTIFERROMAGNETIC NiO, CoO, AND MnO

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ABSTRACT

The time differential perturbed angular correlation (PAC) of $^{111m}\text{Cd}$ substituted as a dilute impurity into antiferromagnetic NiO, CoO, and MnO has been observed. The following magnetic fields are found at the Cd nucleus (4°K): NiO (191.9 ± 2.5 kOe), CoO (170.8 ± 3.0 kOe), MnO (194.7 ± 2.5 kOe). They are compared with the Cd hyperfine fields in the antiferromagnetic perovskites KNiF$_3$/Cd, KCoF$_3$/Cd and RbMnF$_3$/Cd reported earlier. The various interactions leading to supertransferred hyperfine fields are discussed in detail. The oxides are found to be distinctively more covalent than the fluorides. Fractional spin density parameters $f_{\sigma}$ are inferred for the Co-O ($f_{\sigma} = 7.2\%$) and Mn-O ($f_{\sigma} = 8.1\%$) bond. The latter value disagrees with results obtained by neutron diffraction. The spin density parameters $f_{\sigma}$ of the Mn-F and Mn-O bonds, determined by PAC, are used to recalculate the change $\Delta A_{55}$ of the manganese hyperfine coupling constant $A_{55}^c = A_{55}^d + \Delta A_{55}$ in KMnF$_3$ and MnO due to its magnetic neighbors, originally reported by Huang, where $A_{55}^d$ is the manganese hyperfine coupling constant in the dilute systems KMg(Mn)F$_3$ and Mg(Mn)O. It is found that the coupling constants $A_{55}^c$, determined in this way, lead to zero spin deviations, which are no longer in agreement with those predicted by spin wave theory.
I. INTRODUCTION

In a previous letter\textsuperscript{1} we reported the perturbed angular correlation (PAC) of \textsuperscript{111m}Cd doped into antiferromagnetic KNiF\textsubscript{3}, KCoF\textsubscript{3}, and RbMnF\textsubscript{3}. In these lattices, cadmium (Cd\textsuperscript{2+}) enters substitutionally for a transition metal ion. It is octahedrally surrounded by six magnetic ions all belonging to the same sublattice. Spin density is transferred into Cd\textsubscript{s} orbitals, causing a hyperfine field at the Cd nucleus. This field perturbs the angular correlation of the $\gamma$-$\gamma$ cascade of \textsuperscript{111m}Cd. In a time-differential PAC experiment the perturbation is directly observable as a periodic oscillation of the intensity of the second $\gamma$ radiation.

It is well known that the anisotropic part of the ligand (fluorine) hyperfine interaction is determined by the difference $f_{\sigma} - f_{\pi}$ of spin density in fluorine $p_{\sigma}$ and $p_{\pi}$ orbitals. To obtain the covalency parameters $f_{\sigma}$ and $f_{\pi}$ separately, another interaction must be measured, unless the electronic configuration of the transition metal ion permits spin transfer only into either $p_{\sigma}$ or $p_{\pi}$ orbitals alone. Using the known covalency parameter $f_{\sigma}$ (Ni - F) of the Ni\textsuperscript{2+} - F\textsuperscript{-} bond,\textsuperscript{2} we obtained from the ratio of the hyperfine fields at the Cd site in RbMnF\textsubscript{3}/Cd and KNiF\textsubscript{3}/Cd a new estimate for $f_{\sigma}$ (Mn - F), which is considerably larger than an earlier value inferred from neutron diffraction. In our letter\textsuperscript{1} we suggested that not only for fluorides but also for the divalent oxides (NiO, MnO) the spin density parameters $f_{\sigma}$ (Ni - O) and $f_{\sigma}$ (Mn - O) determined by neutron diffraction seem to be too small. Recently, this has been verified by Freund et al.\textsuperscript{3} who measured the \textsuperscript{17}O-ENDOR in Mg(Ni\textsuperscript{2+})\textsuperscript{17}O. They report a value for $f_{\sigma}$ (Ni - O) which is more than twice as large as the estimate obtained by neutron diffraction.\textsuperscript{4} Comparing the hyperfine field at the Cd nucleus in NiO/Cd with those found for MnO/Cd and CoO/Cd, we
estimate the covalency parameters $f_\sigma$ for the Co - O and Mn - O bond to be almost as large as the value $f_\sigma$ (Ni - O).

However, in using PAC to determine covalency parameters, we make certain assumptions about how spin density is transferred from the magnetic ion into the s orbitals of Cd$^{2+}$. We will discuss the various mechanisms in detail by comparing the hyperfine fields found at the Cd site in NiO and KNiF$_3$. Because of symmetry only the six next-nearest metal (Ni$^{2+}$) ions which octahedrally surround the Cd impurity in NiO/Cd contribute to the measured hyperfine interaction. Although NiO and KNiF$_3$ have different crystallographic and magnetic structures, the spin transfer occurs in both cases along linear Ni$^{2+}$ - F$^-$ - Cd$^{2+}$ resp. Ni$^{2+}$ - O$^{2-}$ - Cd$^{2+}$ bonds. The spin densities in the s and p orbitals of the intervening anion are known unambiguously from NMR ($^{19}$F)$^2$ and ENDOR ($^{17}$O)$^3$ This is a rather favorable situation.

Supertransferred hyperfine interactions have been measured using a variety of techniques, including NMR, ENDOR, and Mössbauer. However, in most cases the systems are too complicated to allow a detailed comparison between experiment and theory. The notable exception are the $^{27}$Al ENDOR measurements of Taylor and Owen$^5$ in LaAl(Fe)O$_3$ and LaAl(Cr)O$_3$. Here the spin transfer occurs along the 180$^\circ$ Fe$^{3+}$ - O$^{2-}$ - Al$^{3+}$ bonds. The authors obtained good agreement between experimental and calculated values of the isotropic Al hyperfine interaction constant. The main contribution is due to the overlap of the O$^{2-}$ $2p_g$ function with the outermost filled s-shell (2s) of Al$^{3+}$. Our analysis of the Cd hyperfine fields, which follows closely their approach, supports this point.
II. EXPERIMENTAL

A. Detector System

The spectra were taken with a $\gamma-\gamma$ coincidence fast-slow multidetector system. It was designed for high counting efficiency and good time resolution needed in time differential PAC experiments. Each of the 8 detectors (photomultiplier-tubes RCA 8850, selected for minimal gain shifts at high counting rates, NaI(Tl) scintillators, $1 \times 1\frac{1}{2}''$) could be used as a START and STOP detector. A total of 16 different spectra were taken, eight $180^\circ$ and eight $90^\circ$ combinations, which were chosen in such a way that the ratio of the intensities of the second $\gamma$ radiation $W(180^\circ)/W(90^\circ)$ was independent of counter efficiencies and the lifetime of the intermediate state as described earlier.\(^6\) The fast (anode) pulses were shaped using constant fraction discriminators of the type described by Maier.\(^7\) The discriminator output pulses were fed into a high speed coincidence circuit, similar to that reported by Gerholm.\(^8\) This greatly reduces the input rate to the TAC. The slow (dynode) signals were processed in the conventional way.\(^6\) A fast-slow coincidence circuit allowed to suppress unwanted combinations including triple- and quadruple-coincidences to better than 0.05% even at high counting rates. In a typical experiment the total input rate (sum of all anode outputs) was 400-500 kc/sec. A typical time resolution ($^{22}\text{Na}, 511-511$ keV, $1 \times 1\frac{1}{2}''$ NaI(Tl)) is 1050-1150 psec (fwhm). The counting efficiency was improved by a factor of 4-6 compared to the setup described earlier.\(^6\) Details of the multidetector system will be given elsewhere.

B. Sample Preparation

$^{111m}\text{CdO}$ was obtained by neutron irradiation of $^{110}\text{CdO}$ in the U. C. TRIGA reactor. Because of the high vapor pressure of CdO at the melting points of
NiO, CoO, and MnO, all attempts failed to dope the transition metal oxide by fusing it with CdO.

The samples were prepared by coprecipitation of the corresponding hydroxides or basic carbonates. All operations were done in an inert atmosphere (N₂, glove bag). The precipitates were filtered off, thoroughly washed and transferred to a Pt-boat. They were dried and decomposed by heating in a stream of N₂. Subsequently the oxides were cooled to RT under N₂ or H₂.

As can be seen from Fig. 1, the spectrum shows the periodic pattern typical for a pure magnetic interaction of a polycrystalline sample. The decrease in amplitude (damping) means that the distribution of the hyperfine fields obtained exceeds the natural linewidth. The different methods of coprecipitation always yield (for a particular oxide) the same (center) frequency but the width of the distribution depends on the particular method employed. Best results were obtained in the following way:

NiO: precipitation as a basic carbonate (RT, pH 9.5 - 10.0) using a solution of Na₂CO₃.
CoO: precipitation as basic carbonate (RT, pH 8.5 - 8.7) using a solution of (NH₄)₂CO₃.
MnO: precipitation as hydroxide (95°C, pH 12 - 14) using a solution of NaOH.

C. Data Analysis

Above their Neel temperatures the divalent oxides NiO(Tₙ ≈ 520°K), CoO(Tₙ ≈ 293°K) and MnO(Tₙ ≈ 118°K) have the rock salt structure. Cd²⁺ enters substitutionally for a transition metal ion. It is surrounded by a regular
octahedron of \( O^{2-} \) anions. Because of symmetry, in the antiferromagnetic state the 12 nearest magnetic ions do not contribute to the observed isotropic supertransferred hyperfine interaction. This can be seen very easily by considering one of the \( O^{2-} \) anions next to the dopant \((Cd^{2+})\). It is octahedrally surrounded by 6 cations, where transition metal ions on opposite corners, have antiparallel spins. Thus only the effect of the magnetic ion which is linked to the \( Cd^{2+} \) by a \( 180^\circ \) \( Me^{2+} - O^{2-} - Cd^{2+} \) bond does not vanish by symmetry. There are 6 such next-nearest magnetic ions—all belonging to the same sublattice—which octahedrally surround the dopant. Thus for the supertransferred hyperfine interaction the divalent oxides \( NiO, CoO, MnO \) constitute the same local environment around the dopant \((Cd^{2+})\) as the perovskites \( KNiF_3, KCoF_3, \) and \( RbMnF_3 \). Whereas the 12 nearest cations do not contribute to the unpaired spin density in \( Cd^{2+} \) s orbitals, they give rise to a dipolar field at the \( Cd \) nucleus. \( MnO \) and \( NiO \) have the same magnetic structure, consisting of ferromagnetic \((111)\) planes coupled antiparallel to one another. The spin axes is parallel to the \((111)\) planes. In antiferromagnetic \( MnO \), Lines et al.\(^{10} \) calculated the component of the dipolar field parallel to the spin axes to be +7.67 kOe, at a manganese site and pointing in the same direction as the magnetic moment of the \( Mn^{2+} \) under consideration. Hence, the component of the dipolar field at the \( Cd^{2+} \) nucleus parallel to the spin axis points in the direction of the supertransferred spin density in \( Cd \) s orbitals. Therefore, the nucleus sees the difference \( H_{\text{eff}} = H_{hf} - H_d \) of the hyperfine and dipolar field. The dipolar field in \( NiO \) \((H_d = 4.2 \text{ kOe})\) was obtained from the value reported by Lines et al.\(^{10} \) for \( MnO \), taking the different lattice constants and magnetic moments into account.
The magnetic structure of CoO is not known unambiguously. The structure originally proposed by Roth\(^{11}\) is closely related to the structure observed in antiferromagnetic NiO and MnO. The spin axis lies in the (110) plane tilted by an angle of 27.4\(^\circ\) with respect to the (tetragonal) c axis.\(^{12}\) Another multi spin-axis structure has been proposed by van Laar.\(^{12}\) However, this ambiguity does not affect the supertransferred hyperfine interaction, both magnetic structures leading to the same spin density in Cd s orbitals. The dipolar field, which is a small correction, is calculated adopting the structure proposed by Roth.\(^{11}\) We neglect that the spins are tilted out of the (111) plane by about 8\(^\circ\) and obtain \(H_d\) (CoO) = 6.1 kOe using for the moment of Co\(^{2+}\) the value 3.52 \(\mu_B\) given by van Laar.\(^{12}\)

As it is well known, with the magnetic transition a crystallographic distortion of the divalent oxides occurs. NiO and MnO become rhombohedral, CoO tetragonal. However, these distortions are usually not large enough to affect the PAC spectra. This was found earlier in KFeF\(_3\)/Cd and KCoF\(_3\)/Cd\(^{13,1}\) which undergo at the Néel temperature a rhombohedral, respectively tetragonal distortion.

The spectra shown in Fig. 1 are fitted to the perturbation factor

\[
A_{22} G_{22}(t) = A_{22} \left\{ 1 + 2 \cos (2\pi V_L \cdot t) e^{-|\pi \cdot \sigma \cdot t|} + 2 \cos (4\pi V_L \cdot t) e^{-|2\pi \cdot \sigma \cdot t|} \right\}
\]

where \(V_L = g \cdot \beta_H \cdot N \cdot N_{\text{eff}}\) is the Larmor frequency of the \(^{111m}\)Cd nucleus in the 247 keV state, and a Lorenz distribution of hyperfine fields has been assumed, causing a corresponding spread of Larmor frequencies.

\[
f(\nu) = \frac{2}{\pi \cdot \sigma} \cdot \frac{1}{1 + \frac{(4/\sigma^2)(\nu - V_L)^2}{1}}
\]
σ is the full width at half maximum. In this way the following fields at the Cd nucleus have been obtained:

\[ \text{NiO (4°K)} = 191.1 \pm 2.5 \text{ kOe} \]
\[ \text{CoO (4°K)} = 170.8 \pm 3.0 \text{ kOe} \]
\[ \text{MnO (4°K)} = 194.7 \pm 2.5 \text{ kOe} \]

In calculating the hyperfine fields the new value \(^{(14)}\) for the g factor of the 247 keV state in \(^{111}\)Cd \(g = -0.306\) was used. The corresponding hyperfine fields obtained after correction for the dipolar field, are given in Table I, together with the hyperfine fields observed in KNiF\(_3\)/Cd, KCoF\(_3\)/Cd, and RbMnF\(_3\)/Cd, reported earlier.\(^1\)
III. DERIVATION OF $f_0$ VALUES

The hyperfine fields at nuclei of Cd substituted in antiferromagnetic 
$\text{KNiF}_3$ and $\text{NiO}$ are discussed below in terms of the simple 3-atom model,

$\text{Ni}^{2+} - L - \text{Cd}^{2+}$ ($L = F^-, O^{2-}$). This is analogous to the approach used by Taylor 
and Owen to explain the $^{27}\text{Al}$ hyperfine interaction in $\text{LaAl(Fe}^{3+})O_3$, measured 
by ENDOR. Only orbitals with $C_\infty$ rotational symmetry around the bond axis 
need to be considered, that is, $d_{z^2}$ for $\text{Ni}^{2+}$, $2s$, $2p_\sigma$ for $F^-$, $O^{2-}$ and $4s$, 
$5s$ for $\text{Cd}^{2+}$ (Fig. 2). In this analysis only the outermost closed $s$ shell will be 
considered for both the anion and cadmium. The remaining closed $s$ shells 
are taken as belonging to the core and are regarded as being unaffected by 
neighboring ions. Because of uncertainties in the ionic wavefunctions 
involved, this seems to be more realistic than calculating the overlap effects 
with all inner core ($s$) electrons, which would tend to give considerable 
contributions of alternating sign. This approximation, although commonly made, 
is one of the least satisfactory features of our interpretation. It would be 
highly desirable to test it by ab initio calculations. Finally, the covalency 
of the Cd-$F$ or Cd-$O$ bond is allowed for by including transitions to the 5s 
orbital.

It is well known that spin density is transferred to a ligand $p_\sigma$ orbital 
by overlap and covalency of the Ni-$F$ or Ni-$O$ bond. In molecular orbital 
theory, this is taken into account by forming the bonding and antibonding 
orbitals:

\[
\psi_b = N_b (|p_\sigma\rangle + \gamma_\sigma |d_{z^2}\rangle) \\
\psi_a = N_a (|d_{z^2}\rangle - \lambda_\sigma |p_\sigma\rangle)
\]
where, through terms of first order,

\[ \lambda_0 \approx \gamma_0 + \langle p_0 | d_{z^2} \rangle . \]

In the configuration-interaction method used by Taylor and Owen, \(^5\) covalency is introduced by adding excited (charge transfer) states into the pure ionic ground-state wavefunction,

\[ \psi = \psi_{\text{ion}} + \gamma_0 \psi_{\text{ex}} = \frac{N_1}{\sqrt{3!}} \left\{ d_{z^2}^+ 2s^+ 2s^- p_o^+ p_o^- 4s^+ 4s^- \right\} + \frac{\gamma_0 N_2}{\sqrt{3!}} \left\{ d_{z^2}^+ 2s^+ 2s^- p_o^+ d_{z^2}^- 4s^+ 4s^- \right\} \]

Here the parentheses represent a Slater determinant. The second normalized wavefunction corresponds to the configuration \( \text{Ni}^+ - \text{F}^0 \). Using for \( \text{Ni}^{2+}, \text{F}^- \) or \( \text{O}^{2-} \) and \( \text{Cd}^{2+} \) the orbitals mentioned above, the total wavefunction for the \( \text{Ni} - \text{L} - \text{Cd} \) moiety can be represented by \(^5\)

\[ \psi = N_0 \left( \frac{N_1}{\sqrt{7!}} \right) \left\{ d_{z^2}^+ 2s^+ 2s^- p_o^+ p_o^- 4s^+ 4s^- \right\} + \frac{\gamma_0 N_2}{\sqrt{7!}} \left\{ d_{z^2}^+ 2s^+ 2s^- p_o^+ d_{z^2}^- 4s^+ 4s^- \right\} \]

\[ + \frac{\gamma_5 3}{\sqrt{7!}} \left\{ d_{z^2}^+ 2s^+ 2s^- p_o^+ 5s^- 4s^+ 4s^- \right\} + \frac{\gamma_5 N_4}{\sqrt{7!}} \left\{ d_{z^2}^+ 2s^+ 2s^- 5s^+ 4s^+ 4s^- \right\} \]  

(1)

Here the \( d_{z^2} \) functions belong to Ni, the \( p_o \) and 2s functions to O or F, and the 4s and 5s functions to Cd. Only one-electron transfer processes are taken into account. The hyperfine field at the Cd nucleus is calculated as the matrix element \( \langle \psi | (S - S) h \delta(r) s_z | \psi \rangle \), where the effects of all six bonds are included. Here \( \langle S \rangle \) is the correction for the zero point spin deviation. It can be calculated as \( \langle S \rangle \approx S - \frac{1}{2z} (z = 6) \). The matrix elements between
Determinental wavefunctions composed of nonorthogonal orbitals are evaluated using the method described by Slater. The hyperfine interaction with a ligand nucleus is of second order \((\nu \lambda_0^2)\), and the supertransferred hyperfine fields are of \(4^{th}\) order. Evaluating the matrix element to that order, one obtains

\[
H_{hf} = 6 \frac{\langle s \rangle}{s} H_{4s,4s} \cdot \left( \lambda_0 \langle p_0 | 4s \rangle + \lambda_2 \langle 2s | 4s \rangle \right)^2
\]

\[
- H_{4s,5s} \left( 2 \gamma_5 \lambda_0 \lambda_5 \langle 2s | 4s \rangle + \gamma_5 \lambda_0 \langle p_0 | d z^2 \rangle \langle p_0 | 4s \rangle + \gamma_5 \gamma_5 \langle p_0 | d z^2 \rangle \langle p_0 | 4s \rangle \right)
\]

where

\[
H_{4s,4s} = - \frac{8\pi}{3} \psi_4^2(0), \quad H_{4s,5s} = - \frac{8\pi}{3} \psi_4^2(0) \psi_5(0)
\]

The overlap integrals were calculated by using free-ion wavefunctions and hard-sphere radii to estimate internuclear distances. For \(\langle Ni^{2+} d z^2 | F^- P_0 \rangle\) the Ni-F distance in KNiF\(_3\) was used, and for \(\langle F^- P_0 | Cd^{2+} 4s \rangle\) we took the Cd-F separation in the isomorphous compound KCdF\(_3\). In the same manner the integrals \(\langle Ni^{2+} d z^2 | 0^2- P_0 \rangle\) and \(\langle 0^2- P_0 | Cd^{2+} 4s \rangle\) were calculated for \(d = 2.088\) Å (Ni-O) and \(d = 2.3437\) Å (Cd-O). The integrals are listed in Tables I and II, together with the corresponding ones for Co\(^{2+}\) and Mn\(^{2+}\). Clementi's free-ion wavefunctions were used for Ni\(^{2+}\) (3d\(^8\)), Co\(^{2+}\) (3d\(^7\)), Mn\(^{2+}\) (3d\(^5\)), and F\(^-\). For cadmium we used Mann's wavefunction (4s) of neutral Cd. Since 4s is an inner orbital, the error in taking the neutral atom, rather than Cd\(^{2+}\) wavefunction is expected to be small. For O\(^{2-}\), we used the functions given recently by Yamashita et al., obtained from a band structure calculation of MgO, in which the charge density around the O\(^{2-}\) was afterwards represented by a localized (2p) function. The
numerical values given in Table X of Ref. 20 were supplemented by graphical interpolation. The new $\sigma_2^2$ function is believed to be preferred over the original Watson function (+2 well), and is more contracted, leading to smaller overlap integrals.

The quantities $H_{4s,4s} = -\frac{8\pi}{3} \beta e \psi^2_{4s}(0)$, $H_{4s,5s} = -\frac{8\pi}{3} \beta e \psi_{4s}(0) \psi_{5s}(0)$, and $H_{5s,5s} = -\frac{8\pi}{3} \beta e \psi^2_{5s}(0)$ can be evaluated using the starting values of the corresponding wavefunctions listed in Table III of Ref. 19. In this way one obtains for the hyperfine field of a single unpaired electron in the 5s shell $H_{5s,5s} = -3.6$ MOe. This agrees very poorly with an earlier estimate of -7.14 MOe made from experimental atomic hyperfine coupling constants. A value of -7.2 MOe is obtained by extrapolation of the fields for In$^{3+}$ (-11.4 MOe), Sn$^{4+}$ (-15.3 MOe) and Sb$^{5+}$ (-18.9 MOe) given by Khoi LeDang et al. This discrepancy is actually expected because the wavefunctions in Ref. 19 are non-relativistic, and are based on a point nucleus. A total correction factor of approximately 1.25 should be applied to $\psi^2(0)$ estimated from these wavefunctions, for cadmium. This would yield an estimate of -4.5 MOe for $H_{5s,5s}$, still far short of the empirical value of -7.14 MOe. Two other effects are known: both have the correct sign to narrow this gap. First, the wavefunctions in Eq. (8) pertain to neutral Cd. $H_{5s,5s}$ will certainly be larger in Cd$^+$ (for which the atomic hfs constant was measured) and in Cd$^{2+}$ (the species under study in the present work). Second, core polarization will be present. If these effects could be properly included, and relativistic wavefunctions were used, the experimental value of -7.14 MOe could probably be duplicated. Lacking this, we shall simply use for $H_{5s,5s}$ the estimate of -7.14 MOe obtained from experimental data. We shall scale the calculated values for $H_{4s,4s}$ (-63.6 MOe) and $H_{4s,5s}$ (+15.1 MOe) by assuming that they are off by the same factor (7.18/3.6)
as $H_{5s,5s}$. This assumption is certainly reasonable, because the matrix element of the operator $-\frac{8\pi}{3} e^0 \delta(r) s_z$ with a 4s or 5s H-F function is determined only by that part of the wavefunction which corresponds to a 1s orbital in a Slater-orbital expansion. In addition, the relativity correction is independent of the principal quantum number. In this way, we obtain $H_{4s,4s} = -126$ MOe and $H_{4s,5s} = +30$ MOe. Here and in the following discussion we shall quote the values of these field estimates to more significant figures than their absolute accuracy warrants, in order to preserve their relative values and avoid roundoff errors. We estimate the absolute accuracy as $\sim 10\%$ on the basis of the above discussion.

Using the spin densities $f_\sigma = 3.8\%$, $f_s = 0.54\%$ (KNiF$_3$) and $f_\sigma = 8.5\%$, $f_s = 0.7\%$ (Mg(Ni)$_{17}$O) determined by NMR$^2$ and ENDOR$^3$, the following covalency parameters are obtained:

\[
\begin{align*}
\lambda_\sigma &= -\sqrt{f_\sigma} = -0.195 \\
\gamma_\sigma &= \lambda_\sigma - \langle p_\sigma |d_2^z \rangle = -0.131 \quad \text{(Ni-F)} \\
\lambda_s &= +\sqrt{f_s} = +0.073 \\
\lambda_\sigma &= -\sqrt{f_\sigma} = -0.292 \\
\gamma_\sigma &= \lambda_\sigma - \langle p_\sigma |d_2^z \rangle = -0.229 \quad \text{(Ni-O)} \\
\lambda_s &= +\sqrt{f_s} = +0.084
\end{align*}
\]

The covalency parameters $\gamma_{5s}$ for the Cd-F and Cd-O bond are not known. They are taken to be the same as the parameter $\gamma_\sigma$ for Ni-F and Ni-O bond, $\gamma_{5s} = |\gamma_\sigma| = 0.131$ (Cd-F), $\gamma_{5s} = |\gamma_\sigma| = 0.229$ (Cd-O).
Using these values we obtain for the hyperfine field

\[ |H_{\text{hf}}|_{\text{KNiF}_3/\text{Cd}} = 92 \text{ kOe} + 20 \text{ kOe} = 112 \text{ kOe} \quad \text{(obs. } 105.7 \pm 1.5 \text{ kOe)} \]

\[ |H_{\text{hf}}|_{\text{NiO/Cd}} = 147 \text{ kOe} + 43 \text{ kOe} = 190 \text{ kOe} \quad \text{(obs. } 197.0 \pm 2.5 \text{ kOe)} \]

\[ \frac{|H_{\text{hf}}|_{(\text{NiO/Cd})}}{|H_{\text{hf}}|_{(\text{KNiF}_3/\text{Cd})}} = \left\{ \begin{array}{ll} 1.7 \text{ (calc)} \quad & \\
1.86 \text{ (obs)} \quad & \end{array} \right. \]

The overlap term \( 6 \cdot \frac{S}{S} \cdot H_{4S,4S} \left( \lambda \langle p_0 | 4s \rangle + \lambda \langle 2s | 4s \rangle \right)^2 \) (\text{KNiF}_3: 92 kOe, \text{NiO: } 147 kOe) contributes most to the calculated fields, the cross term being about 20% of the total field in each case. The close agreement between calculated and observed absolute field values is surprising and in view of the many approximations made, not to be taken very seriously. The good agreement obtained for the ratio of the hyperfine fields in NiO and KNiF\(_3\) is a more critical test, since the uncertainties connected with the absolute values of the quantities \( H_{4S,4S} \) and \( H_{4S,5S} \) tend to cancel between the two compounds.

As Eq. (1) shows only one-electron excitations have been taken into account. Under this assumption, Taylor and Owen could successfully explain the isotropic part of the \( ^{27}\text{Al} \) super-hyperfine interaction. In an analogous manner we obtain close agreement between the calculated and experimentally observed hyperfine fields in KNiF\(_3/\text{Cd}\) and NiO/\text{Cd}. We take this to be an indication that overlap effects with the outermost closed s-shell and the covalency of the bond between the anion and diamagnetic cation are adequate to explain supertransferred hyperfine fields. However, although we have used
experimental data whenever possible, the assumptions made in our numerical calculation are severe enough that we cannot exclude with certainty other mechanisms; i.e. two-electron excitations, as contributing significantly to the supertransferred hyperfine fields.

In Anderson's theory of superexchange, two-electron processes play a crucial role for the exchange interaction between the $d$ electrons of two neighboring magnetic ions. Because of the apparent similarity many authors have invoked analogous transfer mechanisms between the $d$ electrons of a magnetic ion and the outermost empty s-shell of a neighboring (diamagnetic) cation to explain experimentally observed hyperfine fields. However, in most cases either the spin densities at the intervening anion were not known or the spin transfer occurred along non-linear bonds $Me_1 - O^{2-} - Me_2$, thereby posing considerable complications. The discussions of the experimentally observed hyperfine fields can only be qualitative under these conditions, and the inclusion of two-electron transfer mechanisms similar to Anderson's kinetic exchange is rather speculative. A serious attempt to explain the observed fields was made by Huang, et al. These authors calculated the supertransferred hyperfine field at a manganese site in $K\text{MnF}_3$ and $\text{MnO}$. Here spin density is transferred respectively through the linear $\text{Mn}^{2+} - F^- - \text{Mn}^{2+}$ or $\text{Mn}^{2+} - O^{2-} - \text{Mn}^{2+}$ paths. These authors included overlap effects with all closed s-shells and the direct transfer into the empty 4s orbital of $\text{Mn}^{2+}$. The supertransferred hyperfine field effectively increases the manganese hyperfine coupling constant, $55\text{A}$. Using the calculated change $\Delta A^{55}$ of the manganese hyperfine coupling constant and the $^{55}\text{Mn NMR}$ in antiferromagnetic $K\text{MnF}_3$ and $\text{MnO}$, the authors calculated the zero-point spin deviations for
both antiferromagnets. In a subsequent paragraph we will show that the original agreement of the calculated spin deviations with the predictions of spin-wave theory obtained by those authors was fortuitous and based on unreasonably small values for the spin density parameters—the only values available at the time. It can no longer be concluded on the basis of this agreement the approach used by these authors to calculate the supertransferred hyperfine field is correct. While two-electron processes might be important for supertransferred hyperfine fields, there is as yet no clear experimental evidence which requires those mechanisms.

Before recalculating the zero-point spin deviations in KMnF$_3$ and MnO, we shall determine the spin density parameters $f_0$(Mn-F) and $f_0$(Mn-O) from the ratio of the measured hyperfine fields at the Cd nuclei. We include a discussion of the possible systematic errors involved in using PAC data to estimate spin-density parameters.

Taking the overlap integrals listed in Tables I and II we calculate, in the same manner as above, the hyperfine fields $H$(KCoF$_3$), $H$(RbMnF$_3$) and $H$(CoO), $H$(MnO). Our new estimates for $f_0$(Co-F), $f_0$(Mn-F), and for $f_0$(Co-O), $f_0$(Mn-O) (Table I) are those values, for which the calculated ratios

$$\left( \frac{H(KCoF_3)}{H(KNiF_3)} \right)_{\text{calc}} \quad \left( \frac{H(RbMnF_3)}{H(KNiF_3)} \right)_{\text{calc}} \quad \text{and} \quad \left( \frac{H(CoO)}{H(NiO)} \right)_{\text{calc}} \quad \left( \frac{H(MnO)}{H(NiO)} \right)_{\text{calc}}$$

are equal to the ratio of the experimentally observed fields. Table I shows, that the $f_0$ values for the 3 fluorides are rather similar, as are the values for the oxides, the latter being about twice as large as the spin densities for the fluorides. This shows that oxides are more covalent than fluorides, and that there is little change in going from Mn$^{2+}$ to Ni$^{2+}$. As mentioned earlier,
neutron diffraction yields a value $27 f_0 (\text{MnO}) = 1.47\%$ which is considerably lower than the value inferred from the PAC data.
IV. RELIABILITY OF THE $f_\sigma$ VALUES

By taking the ratios of the hyperfine fields for two fluorides, uncertainties connected with the absolute values of the quantities $H_{4s,4s}$ and $H_{4s,5s}$ tend to cancel. It is to be expected that this ratio can be calculated even more reliably than the ratio $\frac{H(\text{NiO})}{H(\text{KNiF}_3)}$, for which good agreement was obtained, because the cadmium-anion, that is, the Cd-F bond, is the same for both fields.

In our letter\textsuperscript{1} we reported for $f_\sigma(\text{Mn-F}) = 3.8\%$ and $f_\sigma(\text{Co-F}) = 2.6\%$, values which were obtained by assuming the ratio of the $f_\sigma$ values $f_\sigma(\text{Mn-F})/f_\sigma(\text{Ni-F})$ to be equal to the ratio of the observed hyperfine fields. As can be seen from Eq. (2), this is only approximately true. The cross term is essentially proportional to $|\lambda_\sigma| = \sqrt{f_\sigma}$. This can be seen by adding $-H_{4s,5s} \frac{6 \langle s \rangle}{s} \gamma_{5s} x \langle p_\sigma | d_{z^2} \rangle^2 \langle p_\sigma | 4s \rangle$. Neglecting the term $6 \langle s \rangle \frac{\lambda^2}{s} (2s|4s\rangle)^2$, which is small because both $f_s$ and the overlap integral $\langle 2s|4s \rangle$ are much smaller than the corresponding values for the $p_\sigma$ function one obtains:

$$H_{hf} = 6 \frac{\langle s \rangle}{s} f_\sigma H_{4s,4s} \langle p_\sigma | 4s \rangle^2$$

$$- 6 \frac{\langle s \rangle}{s} 2 \sqrt{f_\sigma} \times \left\{ \sqrt{f_\sigma} (2s|4s\rangle \langle p_\sigma | 4s \rangle) H_{4s,4s} \right\}$$

$$- \gamma_{5s} H_{4s,5s} \times (\langle p_\sigma | 4s \rangle \langle p_\sigma | d_{z^2} \rangle + (2s|4s \rangle \sqrt{f_\sigma}) \right\}.$$

Since $f_s$, $\langle p_\sigma | d_{z^2} \rangle$, $\langle 2s|4s \rangle$, and $\langle p_\sigma | 4s \rangle$ are (essentially) the same for $\text{RbMnF}_3$, $\text{KCoF}_3$, and $\text{KNiF}_3$, the hyperfine field is the sum of two terms $H_{hf} = af_\sigma + b\sqrt{f_\sigma}$ where $a$ and $b$ are independent of the particular fluoride.

If the first term were much larger than the second one, the ratio $H(\text{KCoF}_3)/H(\text{KNiF}_3)$
would be proportional to the ratio of the $f_{\sigma}$ values. If on the other hand the 2\textsuperscript{nd} term were dominant, the ratio of the fields would be proportional to the ratio of $f_{\sigma}^{1/2}$. Since for the fluorides the ratio of the hyperfine fields is near unity, one obtains from each term about the same value for $f_{\sigma}(\text{Co-F})$ and $f_{\sigma}(\text{Mn-F})$. This is the reason why our estimates of $f_{\sigma}(\text{Co-F})$ and $f_{\sigma}(\text{Mn-F})$ are relatively insensitive to the value chosen for the covalency of the Cd-F bond. Furthermore, this explains why the $f_{\sigma}$ values estimated in this paper are just those reported earlier,\textsuperscript{1} where only the first term (proportional to $f_{\sigma}$) had been considered.

Although we obtained good agreement for the calculated and experimentally observed hyperfine fields in KNiF\textsubscript{3} and NiO, two electron transfer mechanisms as we mentioned above, cannot be excluded with certainty. We must therefore investigate how the spin density parameters determined from a relative measurement (the ratio of the hyperfine fields at the Cd nucleus) would be affected, if two electron processes contributed significantly to the supertransferred hyperfine fields. One such process would be the simultaneous jump of 2 electrons into the d\textsubscript{2} orbital of Ni\textsuperscript{2+} and the 5s orbital of Cd\textsuperscript{2+}:

\[
\uparrow\text{Ni}^{2+} - F^{-} \leftrightarrow \text{Cd}^{2+} \rightarrow \uparrow\text{Ni}^{+} - F^{+} - \text{Cd}^{2+} + \text{e}^{-}.
\]

However, the resulting excited state will have a fairly high energy and its admixture into the ground state wavefunction can be neglected. Another transfer process, excited-state admixing into the ionic ground state wavefunction, was proposed by Huang \textit{et al.},\textsuperscript{28} and is closely related to Anderson's\textsuperscript{29} kinetic superexchange mechanism. It consists of a virtual transfer of the single unpaired electron from the magnetic ion into the outermost empty s shell of the neighboring (diamagnetic) cation:
This process can be at least partially visualized as a simultaneous transfer of two electrons, one from the \( (\text{Ni}^{2+})^d_2 \) orbital into the \( (\text{F}^-)_z^2 \) orbital and the other from \( \text{F}^- \) to \( \text{Cd}^{2+}(5s) \). On the other hand, Anderson's kinetic exchange mechanism in \( \text{KNiF}_3 \) consists of the transfer of one d-electron from one \( \text{Ni}^{2+} \) into the d-orbital of the neighboring \( \text{Ni}^{2+} \):

\[
\text{Ni}^{2+}(d_2^2)^+ - \text{F}^- + - \text{Cd}^{2+} + \text{Ni}^{3+} - \text{F}^- + - \text{Cd}^++.
\]

and a corresponding transfer to the left. These two excited states can mix only into the antiferromagnetic ground state, thus lowering its energy relative to the ferromagnetic configuration. As shown by Rimmer, \( \text{a} = \frac{\text{b}}{\text{U}} \)

where \( \text{U} \) is the energy required for the transfer of one electron from one \( \text{Ni}^{2+} \) to the next and \( \text{b} \) is the so-called transfer integral \( \text{a} = \frac{\text{b}}{\text{U}} \).

\[
\text{b} = \left( \lambda_\sigma^2 - \left( p_\sigma |d_2^2\right)^2 \right) (E_d - E_p) - \left( \lambda_s^2 - \left( 2s |d_2^2\right)^2 \right) (E_d - E_s)
\]

In the same way we might obtain an estimate for the transition probability of an electron from the \( d_z^2(\text{Ni}^{2+}) \) orbital into \( \text{Cd}^{2+}(5s) \). We change the expression for \( \text{b} \) to allow for the fact that the transfer involves different orbitals. Assuming the covalency of the Cd-F and Ni-F bonds to be the same, we will change only the energy factors:
For the difference of the orbital energies, e.g. $E_d - E_p$, we take the difference $E(Ni^+ - F^0) - E(Ni^{2+} - F^-)$ obtained by Hubbard, et al.\textsuperscript{31} in the configuration-interaction calculation of KNiF\textsubscript{3}. Changing the corresponding free ion energies, we get from this value an estimate for $E_{5s} - E_p$. Huang\textsuperscript{28} has estimated the energy $U$ for a transfer $\text{Mn}^{2+}(d_2) \rightarrow \text{Mn}^{+}(4s)$ in KMnF\textsubscript{3}. In a similar way, by changing corresponding free-ion energies, we obtain from this value an estimate for $U(\text{Ni}^{2+} d_{z^2} \rightarrow \text{Cd}^{2+} 5s)$:

$$a = \frac{1}{U} \left\{ \left( \lambda_0^2 - \left( \langle p_0 | d_{z^2} \rangle \right)^2 \right) \sqrt{E_d - E_p} \sqrt{E_{5s} - E_p} - \left( \lambda_s^2 - \left( \langle 2s | d_{z^2} \rangle \right)^2 \right) \sqrt{E_d - E_s} \sqrt{E_{5s} - E_s} \right\}.$$ 

For the transfer $\text{Mn}^{2+}(d_{z^2}) \rightarrow \text{Mn}^{+}(4s)$ in KMnF\textsubscript{3}, Huang et al.\textsuperscript{28} reported $a = 1.2 \times 10^{-2}$. However, in their calculation the two terms considered here almost exactly cancel, the value $a = 1.2 \times 10^{-2}$ resulting from a direct 3d-4s interaction.
If we include a transfer of spin density into the Cd 5s orbital by a mechanism analogous to Anderson's kinetic exchange,\(^2\) we obtain mainly the following two additional terms for the hyperfine field at the Cd nucleus:

\[
|6 \frac{\langle S \rangle}{S} a^2 \mathcal{H}_{5s, 5s}| \approx 9 \text{ kOe}
\]

\[
|+6 \frac{\langle S \rangle}{S} 2a(\lambda_0 \langle p_\sigma | 4s \rangle + \lambda_0 \langle 2s | 4s \rangle) \mathcal{H}_{4s, 5s}| \approx 57 \text{ kOe}
\]

Both terms have the same sign and would add to the value 112 kOe listed in Table I. The first (diagonal) term is the hyperfine field due to the spin density in the 5s orbital, while the second is a cross term with the overlap contribution. Since the density of an s orbital at the nucleus drops by more than one order of magnitude in going to the next outer s shell, the direct term is unimportant compared to the cross term. Since \(\lambda_0\) and \(\langle 2s | 4s \rangle\) are much smaller than the corresponding values for the \(p_\sigma\) function, this additional cross term is approximately proportional to \(|\lambda_0| = \sqrt{f_0}\). We have shown above that the hyperfine fields are the sum of two terms proportional to \(f_0\) and \(\sqrt{f_0}\), respectively. The \(f_0\) values determined from the ratio of the experimentally observed hyperfine fields turned out to be rather insensitive to the relative importance of the two terms. Therefore the \(f_0\) values, obtained from the ratio of these fields, would change only slightly, if two-electron excitations contributed significantly to the supertransferred hyperfine field. For example, assuming a direct transfer to Cd\(^{2+}\) (5s) and \(a \approx 1.5 \times 10^{-2}\), \(f_0\) (Co-F) would be reduced only from 2.6% to 2.4%.

Although the spin density parameters are frequently used as a measure of the covalency of a metal-ligand bond, they are also of more basic importance.
As an example we will use our values for \( f_0(Mn-F) \) and \( f_0(Mn-O) \) to recalculate the change of the hyperfine coupling constant \( A_c^{55} \) of Mn\(^{2+}\) in KMnF\(_3\) and MnO, due to a supertransferred hyperfine field.
V. THE RELATION TO ZERO POINT SPIN DEVIATIONS

It is well known that spin-wave theory predicts for three-dimensional antiferromagnets like KMnF$_3$ and MnO a zero spin wave reduction $\frac{S - \langle S \rangle}{S} \approx 3\%$. The usual way to measure the expectation value $\langle S \rangle$ is to observe the $^{55}$Mn-NMR signal in antiferromagnetic KMnF$_3$ or MnO. The resonance frequency $\nu_L$ can be written as $\nu_L = \nu_c + \nu_d$ where $\nu_c$ is the hyperfine coupling constant of Mn$^{55}$ in the concentrated salt KMnF$_3$ or MnO, and $\nu_d$ is a correction due to a dipolar field which is zero for KMnF$_3$ and 8.1 MHz for MnO. Early attempts to observe the zero-point spin deviation used for $\nu_c$ the hyperfine coupling constant $A_c^{55}$ of Mn$^{2+}$ in the corresponding dilute system K$^{55}$MgF$_3$ or Mg$^{55}$O. This led to spin reductions which were too small or even of the wrong sign.

It was pointed out independently by Owen, et al. $^{32}$ and Huang, et al. $^{33}$ that the supertransferred hyperfine field will contribute to the magnetic field at the Mn$^{2+}$ site in KMnF$_3$ and MnO, thus effectively changing the hyperfine coupling constant:

$$A_c^{55} = A_d^{55} + \Delta A_c^{55},$$

where

$$S\Delta A_c^{55} = g_N\alpha N N_H^{\text{hf}}.$$ 

Here $\Delta H^{\text{hf}}$ is the total supertransferred hyperfine field. The spin density transferred into the $s$ orbitals of Mn$^{2+}$ from the six neighboring magnetic ions is antiparallel to the spin of the Mn$^{2+}$ under consideration, but since $s$ electrons and $d$ electrons produce opposite hyperfine fields, the coupling constant $A_c^{55}$ is increased by the amount $\Delta A_c^{55}$. 
Originally Owen, et al. 32 considered only the overlap effect with the outermost closed (3s) shell of Mn$^{2+}$. Huang, et al. 33 included all core (s) orbitals and the direct transfer into the Mn$^{2+}$ 4s orbital. In a subsequent paper Huang, et al. 28 obtained for KMnF$_3$ excellent agreement between the calculated (3.2%) zero spin deviation and that predicted by spin wave theory (3.1%). After correction for a dipolar contribution to the $^{55}$Mn NMR in antiferromagnetic MnO a moderate agreement was found (1.4% compared to 3.1%) for the oxide.

Although Huang's, et al. 28 approach to calculate the supertransferred hyperfine field differs from that used to explain the hyperfine fields in KNiF$_3$/Cd and NiO/Cd, we follow their calculation closely, merely using better experimental data ($f_0^s$(Mn-F) = 3.8%, $f_0^o$(Mn-O) = 8.1%, $\mu_{55}^o$(Mn) = 3.4438 $\mu_B$, $d$(Mn-O) = 2.1665 Å at 4°K 27 and better O$^2-$ wavefunctions. The relevant orbitals are shown in Fig. 3. The same definitions and phases have been used as in Ref. 28. The |ns⟩ functions of Mn(2) are all taken to be positive on the outside. The amplitudes at the origin $\Psi_{ns}^0(0) (n = 1,2,3)$ are evaluated, using Clementi's $^{18}$ Mn$^{2+}$ functions. $\Psi_{4s}^0(0)$ is taken from Ref. 28.

The relevant overlap integrals are given in Table III. The integrals for KMnF$_3$ are those of Ref. 28. For Mn-O the integrals ⟨ns|O$^2-$2s⟩ were calculated using Watson's $^{22}$ O$^2-$2s function (+2 well). For ⟨ns|O$^2-$2p⟩ the functions given by Yamashita $^{20}$ were used. For the supertransferred hyperfine field at Mn(2) due to its right hand side neighbor Mn(1), one obtains: 28

$$|\Delta H| = \frac{8\pi}{3} \beta e \left\{ - \sum_{n=1}^{3} \left( \lambda_o \langle - (ns|p_o) \rangle - \lambda_s \langle ns|s \rangle \right) \Psi_{ns}^0(0) + a\Psi_{4s}^0(0) \right\}^2$$
where
\[ \lambda_\sigma = \sqrt[+]{F_\sigma} > 0 \]
\[ \lambda_s = \sqrt[+]{F_s} > 0 \]
\[ \langle n_s | p_\sigma \rangle < 0 \quad \langle n_s | s \rangle > 0 \]
\[ A + i \frac{a}{s} < 0 \quad s \]
\[ (n_s') > 0 \quad n = 1, 2, 3 \]
\[ a > 0 \]

Adding the contributions from all six surrounding magnetic ions, one obtains: 28
\[ \Delta H_{\text{tot}} = \sum_{n=1}^{3} \Delta H_{n_s,n_s} + \sum_{n \neq m=1}^{3} \Delta H_{n_s,m_s} + \Delta H_{4s,4s} + \sum_{m=1}^{3} \Delta H_{m_s,4s} \]

where the following definitions are used: 28
\[ \Delta H_{n_s,n_s} = +16\pi \beta_e \psi_{n_s}(0) \left\{ \lambda_\sigma (-\langle n_s | p_\sigma \rangle) - \lambda_s \langle n_s | s \rangle \right\}^2 \quad n = 1, 2, 3 \]
\[ \Delta H_{4s,4s} = +16\pi \beta_e \psi_{4s}(0) \quad a^2 \]
\[ \Delta H_{m_s,ns} = +32\pi \beta_e \psi_{ms}(0) \psi_{ns}(0) \left\{ \lambda_\sigma (-\langle ms | p_\sigma \rangle) - \lambda_s \langle ms | s \rangle \right\} \]
\[ \times \left\{ \lambda_\sigma (-\langle ms | p_\sigma \rangle) - \lambda_s \langle ms | s \rangle \right\} \quad m, n = 1, 2, 3 \quad m \neq n \]
\[ \Delta H_{ms,4s} = -32\pi \beta_e \psi_{ms}(0) \psi_{4s}(0) \quad a \cdot \left\{ \lambda_\sigma (-\langle ms | p_\sigma \rangle) - \lambda_s \langle ms | s \rangle \right\} \]

The different contributions to the total supertransferred hyperfine field are listed in Table IV. They are calculated using for the direct transfer parameter \( a \) the values \( a = 1.2\% \) (KMnF$_3$) and \( a = 2.1\% \) (MnO) given in Ref. 28.
The $^{55}\text{Mn}$ NMR ($\nu_L^{55}\text{(KMnF}_3) = 676 \pm 3 \text{ MHz}$) in antiferromagnetic KMnF$_3$ has been observed by Minkiewicz and Nakamura.$^{34}$ Montgomery, et al.$^{35}$ extrapolated a value of $^{55}A_d = -91.64 \times 10^{-4} \text{ cm}^{-1}$ for KMg(Mn)F$_3$ adjusted to a lattice constant appropriate for KMnF$_3$. Using the calculated value $\Delta H_{\text{tot}}$ for the supertransferred hyperfine field in KMnF$_3$, we obtain for the zero spin wave reduction

$$\frac{S - \langle S \rangle}{S} = \frac{A_{55} S - A_{55} \langle S \rangle}{A_{55} S} = \frac{|A_{55}S + g_{55} \beta_{55} | \Delta H_{\text{tot}}| - \nu_L^{55}}{|A_{55}S + g_{55} \beta_{55} | \Delta H_{\text{tot}}|} = 5.3\% \text{ (KMnF}_3).$$

Lines, et al.$^{10}$ determined the $^{55}\text{Mn}$ NMR in antiferromagnetic MnO to be $617.8 \pm 0.1 \text{ MHz}$. After correction for the dipolar field one obtains

$$\nu_L^{55}\text{(MnO)} = 625.9 \pm 0.2 \text{ MHz}.$$  
Walsh$^{36}$ obtained for the $^{55}\text{Mn}$ hyperfine coupling constant in Mg(Mn)O, $^{55}A_d = -81.55 \times 10^{-4} \text{ cm}^{-1}$. Using the value 67.6 kOe for the total supertransferred hyperfine field, one obtains:

$$\frac{S - \langle S \rangle}{S} = 8.3\% \text{ (MnO)}.$$

Since spin-wave theory is known to be approximately correct, these zero-point spin wave reductions are far too large. In the oxide the discrepancy would have been even more serious if we had used the more expanded $O^{2-}(2p)$ function of Watson.$^{22}$ It follows that the excellent (KMnF$_3$: 3.2%) to moderate (MnO: 1.4%) agreement with spin-wave theory originally obtained by Huang$^{28}$ was fortuitous because it was based on the inadequate experimental data which was available at that time. It can no longer be concluded that the approach for calculating the supertransferred hyperfine field used by those authors is correct. Therefore it is no longer clear whether a direct transfer into the outermost unoccupied
orbital is important or not. As can be seen from Table IV, the orthogonalization of the ligand wavefunctions 2s, and 2p_y to all inner s shells leads to large contributions of alternating signs. We doubt that this is physically reasonable.

If we took the 1s and 2s functions of Mn^{2+} to belong to the core, then the dominant term would be \( \Delta H_{3s,3s} = 66.9 \) kOe. If we include the direct transfer (\( a = 2.1\% \)) or the covalency of the \( O^2-(p_y) - Mn^{2+}(4s) \) bond, this value is raised further. It follows that the approach which led to good agreement between experimental and calculated supertransferred hyperfine fields in KNiF\(_3\)/Cd and NiO/Cd cannot account for the zero-point spin deviation either. However the corrections to the Mn\(^{2+}\) hyperfine coupling constant which have to be made in going from the dilute system \( A_{d}^{55} \) to the concentrated salt \( A_{c}^{55} \) is a more subtle problem, and a successfully calculated spin deviation is less direct evidence than the calculation of an experimentally observed hyperfine field at a nominally diamagnetic cation. It would be difficult to infer from the corrections of the hyperfine coupling constant \( A_{c}^{55} \) how supertransferred hyperfine fields should be accounted for.

We conclude by noticing that omitting the covalency of the \( Mn^{2+}(4s) - F^{-}(O^2-)p_y \) moiety and by omitting direct transfer (\( a = 0 \)) but including all other s shells, good agreement with spin wave theory would be obtained (3.6% in KMnF\(_3\)), (3.2% in MnO). But until supertransferred hyperfine interactions are better understood, we would view this result with suspicion and consider it to be fortuitous.
VI. CONCLUSIONS

The perturbed angular correlation of $^{111m}$Cd doped into antiferromagnetic NiO, CoO and MnO has been observed and the hyperfine fields at the Cd nucleus determined. They are compared with those found in KNiF$_3$/Cd, KCoF$_3$/Cd, and RbMnF$_3$/Cd.

Using the spin density parameters $f_\sigma$(Ni-F), $f_s$(Ni-F), $f_\sigma$(Ni-O), $f_s$(Ni-O) known from NMR (KNiF$_3$) and ENDOR (Mg(Ni$^{2+}$)$_{17}$O) the hyperfine fields at the Cd nucleus in KNiF$_3$/Cd and NiO/Cd have been calculated. Good agreement between calculated and experimentally observed fields was obtained taking only one-electron excitation into account. From the ratios of the hyperfine fields $H$(CoO)/$H$(NiO) and $H$(MnO)/$H$(NiO), new estimates for the spin density parameters $f_\sigma$(CoO) and $f_\sigma$(MnO) have been obtained. Spin density parameters determined in this way are found to be insensitive both to the values of various only approximately known parameters and to the relative importance of different transfer mechanisms.

The spin density parameters $f_\sigma$(Mn-F) and $f_\sigma$(Mn-O) given in this paper are used to recalculate the change of the $^{55}$Mn hyperfine coupling constant due to the influence of its magnetic neighbors, reported earlier by Huang, et al. The corrected hyperfine coupling constants $^{55}A_c$ are used to determine the zero spin deviations in KMnF$_3$ and MnO. It is found that the original agreement obtained by Huang, based on erroneous values for $f_\sigma$(Mn-F) and $f_\sigma$(Mn-O) obtained by neutron diffraction was fortuitous.
ACKNOWLEDGMENTS

We are indebted to Dr. P. Freund and Dr. J. Owen for making their ENDOR data on \( \text{Mg(Ni}^{2+})^{17}\text{O} \) available to us prior to publication. We thank Dr. M. Maier for his invaluable assistance in setting up the multi-channel detector system.
FOOTNOTES AND REFERENCES

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13. H. H. Rinneberg and D. A. Shirley, to be published.
### Table I

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<th>KNiF₃</th>
<th>KCoF₃</th>
<th>RbMnF₃</th>
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<th>CoO</th>
<th>MnO</th>
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<td>0.54%</td>
<td>0.50%</td>
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<td>3.8%*</td>
<td>8.5%</td>
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<td>8.1%*</td>
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<td>(79.3 kOe)</td>
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<td>(170.9 kOe)</td>
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*The hyperfine fields in parentheses were used to determine the spin density parameters marked by a star *.
## Table II

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</table>
Table III

<p>|        | ( \langle 1s|p_\sigma \rangle ) | ( \langle 2s|p_\sigma \rangle ) | ( \langle 3s|p_\sigma \rangle ) | ( \langle 1s|s \rangle ) | ( \langle 2s|s \rangle ) | ( \langle 3s|s \rangle ) | ( \lambda_\sigma ) | ( \lambda_s ) |
|--------|-----------------------------------|-----------------------------------|-----------------------------------|----------------|----------------|----------------|----------------|----------------|
| KMnF_3 | -0.0017                           | -0.0131                           | -0.0684                           | +0.0002        | +0.0019        | +0.0147        | 0.195          | 0.071          |
| MnO    | -0.0019                           | -0.0137                           | -0.0730                           | +0.0003        | +0.0027        | +0.0196        | 0.285          | 0.089          |</p>
<table>
<thead>
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<th></th>
<th>$\Delta H_{1s1s}$</th>
<th>$\Delta H_{2s2s}$</th>
<th>$\Delta H_{3s3s}$</th>
<th>$\Delta H_{1s2s}$</th>
<th>$\Delta H_{1s3s}$</th>
<th>$\Delta H_{2s3s}$</th>
<th>$\Delta H_{1s4s}$</th>
<th>$\Delta H_{2s4s}$</th>
<th>$\Delta H_{3s4s}$</th>
<th>$\Delta H_{4s4s}$</th>
<th>$\Delta H_{\text{tot}}$</th>
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<td>KMnF$_3$</td>
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<td>-29.8</td>
<td>3.4</td>
<td>-7.8</td>
<td>14.5</td>
<td>1.9</td>
<td>25.4</td>
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<tr>
<td>MnO</td>
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<td>18.5</td>
<td>66.9</td>
<td>-16.5</td>
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<td>-70.3</td>
<td>9.3</td>
<td>-20.7</td>
<td>39.5</td>
<td>5.8</td>
<td>67.6</td>
</tr>
</tbody>
</table>

*All field values in kOe.*
FIGURE CAPTIONS

Fig. 1. Time differential PAC spectra of $^{111m}$Cd doped into antiferromagnetic NiO, MnO, and CoO.

Fig. 2. Atomic orbitals used for the calculation of the hyperfine field in KNiF$_3$/Cd and NiO/Cd.

Fig. 3. Atomic orbitals involved in the determination of the zero spin deviation in MnO and KMnF$_3$. 
Fig. 1
Fig. 2
Fig. 3
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