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Supertransferred hyperfine interaction: Perturbed angular correlation of ^{111}Cd^m in antiferromagnetic NiO, CoO, and MnO†

H. H. Rinneberg and D. A. Shirley

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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The time-differential perturbed angular correlation of ^{111}Cd^m 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 (191.1 ± 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 oxides are found to be more covalent than the fluorides. From the ratio of the hyperfine fields in MnO:Cd and NiO:Cd a new value of the spin density parameter f_σ(Mn-O) = 8.1% has been estimated.

I. INTRODUCTION

In a previous Letter[1] we reported the perturbed angular correlation (PAC) of ^{111}Cd^m doped into the antiferromagnetic perovskites $KNiF_3$, $KCoF_3$, and $RbMnF_3$. In these lattices, cadmium (Cd^{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 *s* orbitals, causing a hyperfine field at the Cd nucleus. This field perturbs the angular correlation of the γ-γ cascade of ^{111}Cd^m. In a time-differential PAC experiment the perturbation is directly observable as a periodic oscillation of the intensity of the second γ radiation.

Besides PAC, supertransferred hyperfine interactions have been measured using a variety of techniques including NMR, Mössbauer, and electron-nuclear double resonance (ENDOR). The transfer of spin density from the magnetic ions into the *s* shells of a neighboring cation is usually thought to involve the intervening anion. Boekema *et al.*[2] used a molecular-orbital approach to explain the ^{57}Fe hyperfine fields in rare-earth orthoferrites. Taylor *et al.*[3] observed the ^{27}Al ENDOR in LaAl(Fe)O_3 and LaAl(Cr)O_3. These authors discussed the Al hyperfine constant within the framework of a configuration-interaction calculation. A direct transfer of unpaired *d*-electrons to the empty 4*s* shell of a neighboring manganese ion has been considered by Huang *et al.*[4] to calculate the supertransferred hyperfine field in $KMnF_3$ and MnO.

In order to study the influence of the intervening anion on the transfer of spin density we have measured the PAC of ^{111}Cd^m doped into the antiferromagnetic oxides NiO, CoO, and MnO. In Sec. II we give experimental details. Using the configuration-interaction approach of Taylor *et al.*[3] the hyperfine field at the Cd impurity in NiO and $KNiF_3$ is calculated in Sec. III. We conclude with a discussion of the hyperfine fields observed in the remaining oxides and perovskites.

II. EXPERIMENTAL

A. Detector system

The spectra were taken with a γ-γ 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 eight detectors (photomultiplier tubes RCA 8850, selected for minimal-gain shifts at high-counting rates; NaI(Tl) scintillators, $1\times1\frac{1}{2}$ in.) could be used as a start and stop detector. A total of 16 different spectra were taken, eight 180° and 90° combinations, which were chosen in such a way that the ratio of the intensities of the second γ radiation $W(180°)/W(90°)$ was independent of counter efficiencies and the lifetime of the intermediate state as described earlier.[5] The fast (anode) pulses were shaped using constant fraction discriminators of the type described by Maier.[6] The discriminator output pulses were fed into a high-speed coincidence circuit, similar to that reported by Gerholm.[7] This greatly reduces the input rate to the time-to-amplitude converter. The slow (dynode) signals were processed in the conventional way.[5] A fast-slow coincidence circuit permitted the suppression of 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 kHz. A typical time resolution [^{22}Na, 511–511 keV, $1\times1\frac{1}{2}$-in. NaI(Tl)] is 1050–1150 psec [full width at half-maximum (FWHM)]. The counting efficiency was improved by a factor of ~ 4 compared to the setup described earlier.[5]

B. Sample preparation

$^{111}Cd^{m}O$ was obtained by neutron irradiation of ^{110}CdO in the University of California 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.[8] Basic nickel carbonate was precipitated (25 °C, pH 9.5–10.0) using a solution of Na_2CO_3. Basic cobalt carbonate was obtained (25 °C, pH 8.5–8.7) using a solution of $(NH_4)_2CO_3$. $Mn(OH)_2$ was precipitated at 95 °C (pH 12–14) with an aqueous solution of NaOH. In order to avoid oxidation by air all operations were done in an inert atmosphere (N_2, 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 N_2. Subsequently the oxides were cooled to room temperature under N_2 or H_2. Typically, the oxides were doped with 0.1-mol% Cd.

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. Samples showing a minimal amount of damping were prepared in the manner described above.

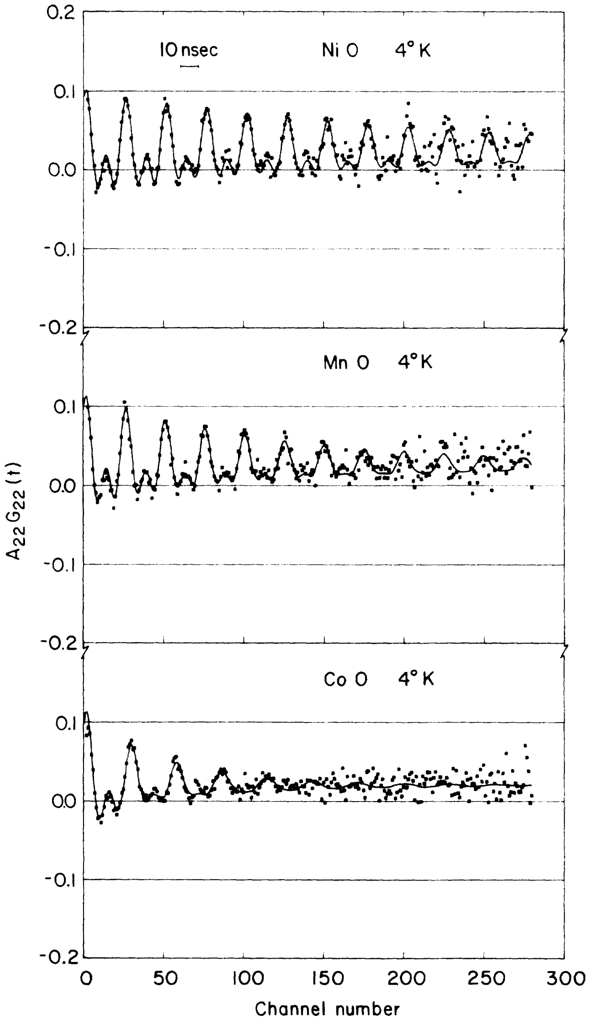

FIG. 1. Time-differential PAC spectra of $^{111}Cd^{m}$ doped into antiferromagnetic NiO, MnO, and CoO.

C. Data analysis

Above their Néel temperatures the divalent oxides NiO ($T_N \approx 520$ °K), CoO ($T_N \approx 293$ °K), and MnO ($T_N \approx 118$ °K) have the rock-salt structure. Cd^{2+} is assumed to enter 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 six 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 an 180° M^{2+}-O^{2-}-Cd^{2+} bond does not vanish by symmetry. There are six 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 are parallel to the (111) planes. In antiferromagnetic MnO, Lines and Jones[9] calculated the component of the dipolar field parallel to the spin axis 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 $H_{\text{int}} = H_{\text{hf}} - H_d$ of the hyperfine and dipolar field. The dipolar field in NiO ($H_d = 4.2$ kOe) was obtained from the value reported by Lines and Jones[9] 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[10] is closely related to the structure observed in antiferromagnetic NiO and MnO. The spin axis lies in the $(1\bar{1}0)$ plane tilted by an angle of 27.4° with respect to the (tetragonal) c axis.[11] Another multi-spin-axis structure has been proposed by Van Laar.[11] 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.[10] We neglect that the spins are tilted out of the (111) plane by about 8° and obtain $H_d(\text{CoO}) = 6.1$ kOe using for the moment of Co^{2+} the value $3.52\mu_B$ given by Van Laar.[11]

As is well known, with the magnetic transition a crystallographic distortion of the divalent oxides occurs. NiO and MnO become rhombohedral and CoO tetragonal. However, the electric field gradients connected with the deviations from cubic symmetry are far too small to be detected by PAC. This was found earlier for $KCoF_3$:Cd which undergoes a tetragonal distortion at the Néel temperature.

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

$$A_{22}G_{22}(t) = \tfrac{1}{5}A_{22}\left[1 + 2\cos(2\pi\nu_L t)e^{-|\pi\sigma t|} + 2\cos(4\pi\nu_L t)e^{-|2\pi\sigma t|}\right],$$

where $\nu_L = g_N\mu_N H_{\text{int}}$ is the Larmor frequency of the $^{111}Cd^m$ nucleus in the 247 keV state, and a Lorenz distribution of hyperfine fields has been assumed, causing a corresponding spread of Larmor frequencies

$$f(\nu) = \frac{2}{\pi\sigma}\,\frac{1}{1+(4/\sigma^2)(\nu-\nu_L)^2}\,.$$

Here, σ is the full width at half-maximum. The internal fields H_{int} (4 °K) obtained in this way are given in Table I together with the hyperfine fields H_{hf} corrected for the dipolar contribution. The new value[12] for the g factor, $g = -0.306$, of the 247-keV state of ^{111}Cd was used to convert the measured frequencies into magnetic field values. In Table I we include the hyperfine fields in the corresponding perovskites reported earlier.[1]

III. DISCUSSION

As mentioned above, only the six second-nearest magnetic neighbors which octahedrally surround the Cd impurity in the antiferromagnetic divalent oxides contribute to the spin density in Cd s orbitals. Similarly in the perovskites, spin density is transferred from the six-nearest magnetic ions octahedrally coordinated with the Cd impurity through linear M^{2+}-F^--Cd^{2+} bonds. Therefore, a direct comparison between the hyperfine fields in the oxides and the corresponding perovskites is possible and should show the influence of the intervening anion. From Table I it is seen, that the hyperfine fields observed in the oxides are about twice as large as in the corresponding fluorides. Qualitatively, if we assume the transfer of spin density through the intervening anion to be the dominant mechanism, then, from the larger unpaired spin density at the Cd impurity in the oxides we expect a larger unpaired spin density at the O^{2-} ion provided the transfer of spin density from the anion into the Cd s shells is not too different for the Cd-O and Cd-F bonds. This transfer occurs through the overlap of the anion p_σ function and the closed Cd s shells, and through charge transfer into the outermost unoccupied $5s$ function. We have calculated the overlap of the F^--$2p_\sigma$ and O^{2-}-$2p_\sigma$ function with the outermost closed $4s$ shell of Cd^{2+}. The overlap integrals are rather similar. The charge transfer from the $2p_\sigma$ function into the Cd $5s$ shell will be larger for the more covalent Cd-O bond compared to the Cd-F bond. However, since the density of a $5s$ function at the nucleus is considerably smaller than that of the $4s$ shell, the

TABLE I. Experimental values for the internal fields H_{int} (4 °K) and hyperfine fields H_{hf}, corrected for a dipolar contribution, at Cd in various antiferromagnetic fluorides[1] and oxides.

	NiO	CoO	MnO	$KNiF_3$	$KCoF_3$	$RbMnF_3$
H_{int} (kOe)	191.1 ± 2.5	170.8 ± 3.0	194.7 ± 2.5	105.7 ± 1.5	74.1 ± 1.5	113.8 ± 1.5
H_{hf} (kOe)	196.0 ± 3.5	176.9 ± 4.0	202.4 ± 3.0	105.7 ± 1.5	74.1 ± 1.5	113.8 ± 1.5

major contribution to the hyperfine field is caused by the 4*s* shell. Therefore, from the experimentally observed hyperfine fields we expect a larger unpaired spin density in the O^{2-}-p_σ function than in the F^--p_σ orbital. This is consistent with recent results obtained by Freund,[13] who measured the ^{17}O ENDOR in $Mg(Ni^{2+})^{17}O$. He obtained for the amount of unpaired spin density $f_\sigma(\text{Ni-O}) = 8.5\%$, whereas $f_\sigma(\text{Ni-F}) = 3.8\%$ is known from the ^{19}F NMR in $KNiF_3$.[14]

In the following we use these experimental values for the spin density at the F^- and O^{2-} intervening anion to calculate the hyperfine field at the impurity in $KNiF_3$:Cd and NiO:Cd. Following the approach taken by Taylor *et al.*[3] to explain the Al hyperfine interaction in $LaAl(Fe)O_3$, we base the calculation on the simple three-atom model Ni^{2+}-L-Cd^{2+} ($L = F^-$, O^{2-}). Only orbitals with rotational symmetry around the bond axis have to be taken into account, that is, d_{z^2} for Ni^{2+}; 2*s*, $2p_\sigma$ for F^-, O^{2-}; and 4*s*, 5*s* for 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 wave functions 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.

It is well known that spin density is transferred to a ligand p_σ orbital by overlap and covalency of the Ni-F or Ni-O bond.[15,16] In molecular-orbital theory, this is taken into account by forming the bonding and antibonding orbitals:

$$\psi_b = N_b(|p_\sigma\rangle + \gamma_\sigma |d_{z^2}\rangle),$$
$$\psi_a = N_a(|d_{z^2}\rangle - \lambda_\sigma |p_\sigma\rangle), \tag{1}$$

where, through terms of first order,

$$\lambda_\sigma \cong \gamma_\sigma + \langle p_\sigma | d_{z^2}\rangle .$$

In the configuration-interaction method used by Taylor *et al.*,[3] covalency is introduced by adding excited (charge transfer) states into the pure ionic-ground-state wave function,

$$\psi = \psi_{\text{ion}} + \gamma_\sigma \psi_{\text{ex}} = (N_1/\sqrt{3!})\{d^+_{z^2} p^+_\sigma p^-_\sigma\} + (\gamma_\sigma N_2/\sqrt{3!})\{d^+_{z^2} p^+_\sigma d^-_{z^2}\} . \tag{2}$$

Here the curly brackets represent a Slater determinant. The second normalized wave function corresponds to the configuration Ni^+-F^0. Using for Ni^{2+}, F^-, or O^{2-} and Cd^{2+}, the orbitals mentioned above, the total wave function for the Ni-*L*-Cd moiety can be represented by[3]

$$\begin{aligned}\psi = N_0[&(N_1/\sqrt{7!})\{d^+_{z^2} 2s^+ 2s^- p^+_\sigma p^-_\sigma 4s^+ 4s^-\}\\ &+\gamma_\sigma(N_2/\sqrt{7!})\{d^+_{z^2} 2s^+ 2s^- p^+_\sigma d^-_{z^2} 4s^+ 4s^-\}\\ &+\gamma_{5s}(N_3/\sqrt{7!})\{d^+_{z^2} 2s^+ 2s^- p^+_\sigma 5s^- 4s^+ 4s^-\}\\ &+\gamma_{5s}(N_4/\sqrt{7!})\{d^+_{z^2} 2s^+ 2s^- 5s^+ p^-_\sigma 4s^+ 4s^-\}] .\end{aligned} \tag{3}$$

Here the d_{z^2} function belongs to Ni, the p_σ and 2*s* functions to O or F, and the 4*s* and 5*s* 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

$$\left\langle \psi \left| 6\frac{\langle S\rangle}{S}\left(-\frac{8\pi}{3}\right) g_e \mu_B \sum_i \delta(r_i) s_{zi} \right| \psi \right\rangle ,$$

where the effects of all six bonds are included. As is well known, Ni^{2+} in an octahedral crystal field has an effective spin $S = 1$ to a good approximation. The factor $\langle S\rangle/S$ is the correction for the zero-point spin deviation. It can be calculated as $\langle S\rangle \approx S - 1/(2z)$ $(z = 6)$.[17] The matrix elements between determinantal wave functions composed of nonorthogonal orbitals are evaluated using the method described by Slater.[18] The hyperfine interaction with a ligand nucleus is of second order $(\sim\lambda^2_\sigma)$, and the supertransferred hyperfine fields are of the fourth order. Evaluating the matrix element to that order, one obtains[3]

$$\begin{aligned}H_{\text{hf}} = 6(\langle S\rangle/S)[&H_{4s,4s}(\lambda_\sigma\langle p_\sigma|4s\rangle + \lambda_s\langle 2s|4s\rangle)^2\\ &- H_{4s,5s}(2\gamma_{5s}\lambda_\sigma\lambda_s\langle 2s|4s\rangle + \gamma_{5s}\lambda_\sigma\langle p_\sigma|d_{z^2}\rangle\langle p_\sigma|4s\rangle\\ &+\gamma_{5s}\gamma_\sigma\langle p_\sigma|d_{z^2}\rangle\langle p_\sigma|4s\rangle)],\end{aligned}$$

where

$$H_{4s,4s} = -\tfrac{8}{3}\pi\mu_B\psi^2_{4s}(0), \quad H_{4s,5s} = -\tfrac{8}{3}\pi\mu_B\psi_{4s}(0)\psi_{5s}(0).$$

The overlap integrals were calculated by using free-ion wave functions and hardsphere radii to estimate internuclear distances. For $\langle Ni^{2+}d_{z^2}|F^-p_\sigma\rangle$ the Ni-F distance in $KNiF_3$ was used, and for $\langle F^-p_\sigma|Cd^{2+}4s\rangle$ we took the Cd-F separation in the isomorphous compound $KCdF_3$. In the same

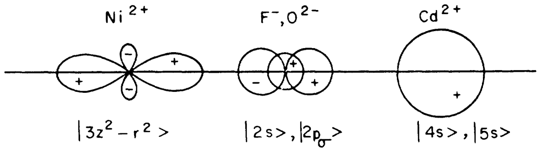

FIG. 2. Atomic orbitals (schematic) used for the calculation of the hyperfine field in $KNiF_3$:Cd and NiO:Cd.

manner the integrals $\langle \mathrm{Ni}^{2+} d_{z^2} | \mathrm{O}^{2-} p_\sigma \rangle$ and $\langle \mathrm{O}^{2-} p_\sigma | \mathrm{Cd}^{2+} 4s \rangle$ were calculated for $d = 2.088$ Å (Ni–O) and $d = 2.3437$ Å (Cd–O). The integrals are listed in Tables II and III together with the corresponding ones for Mn^{2+}. Clementi's[19] free-ion wave functions were used for Ni^{2+} ($3d^8$), Mn^{2+} ($3d^5$), and F^-. For cadmium we used Mann's[20] wave function ($4s$) of neutral Cd. Since $4s$ is an inner orbital, the error in taking the neutral atom, rather than the Cd^{2+} wave function is expected to be small. For O^{2-}, we used the functions given recently by Yamashita *et al.*,[21] 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. 21 were supplemented by graphical interpolation. The new O^{2-} p_σ function is believed to be preferred over[22] the original Watson[23] function (+ 2 well), and is more contracted, leading to smaller overlap integrals.

The quantities $H_{4s,4s} = -\frac{8}{3}\pi\mu_B\psi_{4s}^2(0)$, $H_{4s,5s} = -\frac{8}{3}\pi\mu_B\psi_{4s}(0)\psi_{5s}(0)$, and $H_{5s,5s} = -\frac{8}{3}\pi\mu_B\psi_{5s}^2(0)$ can be evaluated using the starting values of the corresponding wave functions listed in Table III of Ref. 20. 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.[24] 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.*[25] This discrepancy is actually expected because the wave functions in Ref. 20 are nonrelativistic, 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 wave functions, for cadmium.[26,27] 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, $H_{5s,5s}$ 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 wave functions 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[24] 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 $-\frac{8}{3}\pi\mu_B\delta(r)s_z$ with a $4s$ or $5s$ Hartree-Fock function is determined only by that part of the wave function which corresponds to a $1s$ orbital in a Slater-orbital expansion. In addition, the relativity correction is independent of the principal quantum number.[26] 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 ~ 20% on the basis of the above discussion.

Using the spin densities $f_\sigma = 3.8\%$, $f_s = 0.54\%$ ($\mathrm{KNiF_3}$), and $f_\sigma = 8.5\%$, $f_s = 0.7\%$ [$\mathrm{Mg(Ni)\,^{17}O}$] determined by NMR[14] and ENDOR,[13] the following covalency parameters are obtained: $\lambda_\sigma = -\sqrt{f_\sigma} = -0.195$, $\gamma_\sigma = \lambda_\sigma - \langle p_\sigma | d_{z^2} \rangle = -0.131$, $\lambda_s = +\sqrt{f_s} = +0.073$ (Ni-F); $\lambda_\sigma = -\sqrt{f_\sigma} = -0.292$, $\gamma_\sigma = \lambda_\sigma - \langle p_\sigma | d_{z^2} \rangle = -0.229$, $\lambda_s = +\sqrt{f_s} = +0.084$(Ni-O). The covalency parameters γ_{5s} for the Cd-F and Cd-O bond are not known. They are taken to be the same as the parameter γ_σ for the 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 in $\mathrm{KNiF_3}$ (Cd): $|H_{\mathrm{hf}}| = 92$ kOe + 20 kOe = 112 kOe, (obs 105.7 ± 1.5 kOe); and in NiO(Cd): $|H_{\mathrm{hf}}| = 147$ kOe + 43 kOe = 190 kOe, (obs 196.0 ± 3.5 kOe). For the ratio of the hyperfine fields in NiO and $\mathrm{KNiF_3}$ we calcu-

TABLE II. Overlap integrals and spin-density parameters for the calculation of cadmium hyperfine fields H_{hf}. The values in parentheses were used to determine the spin-density parameters marked by a star(*).

	$\mathrm{KNiF_3}$	$\mathrm{RbMnF_3}$	NiO	MnO
$\langle p_\sigma \| d_{z^2} \rangle$	−0.0602	−0.0688	−0.0621	−0.0712
f_s	0.54%	0.50%	0.7%	0.8%
f_σ	3.8%	3.8%*	8.5%	8.1%*
H_{hf} (calc)	112.4 kOe	(121.8 kOe)	189.6 kOe	(196.4 kOe)

TABLE III. Cadmium-anion overlap integrals.

	Cd-F	Cd-O
$\langle p_\sigma \vert 4s\rangle$	+0.0640	+0.0535
$\langle 2s \vert 4s\rangle$	+0.0130	+0.0124

late $|H_{hf}|(\text{NiO Cd})/|H_{hf}|(\text{KNiF}_3\text{ Cd}) = 1.7$ compared to the observed value 1.86. The overlap term $6(\langle S\rangle/S)H_{4s,4s}(\lambda_\sigma\langle p_\sigma|4s\rangle + \lambda_s\langle 2s|4s\rangle)^2$, ($KNiF_3$: 92 kOe, NiO: 147 kOe) contributes most to the calculated fields, the cross term being about 20% of the total field in each case.

There are several sources for errors which could affect the calculated hyperfine fields. The use of free-ion wave functions in a solid is a severe approximation. The Cd-O and Cd-F internuclear distances are not known for Cd doped into NiO and $KNiF_3$, although using the separations found in the corresponding isomorphic cadmium compounds is certainly reasonable. Furthermore, the inclusion of all inner Cd *s* shells into the calculation would probably reduce the calculated values for the hyperfine fields. The charge-transfer parameter γ_{5s} was only estimated. However, as mentioned above, the cross term which is proportional to γ_{5s} does not make the main contribution to the hyperfine field. Furthermore, we cannot exclude a direct spin transfer from the Ni^{2+} d_{z^2} orbital into the Cd 5*s* function. In view of the many approximations made, the close agreement between the calculated and observed hyperfine fields is not to be taken very seriously. The good agreement for the ratio of the hyperfine fields in NiO and $KNiF_3$ is a better 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.

In the following we want to make a new estimate for the spin-density parameter f_σ of the Mn-O bond by comparing the hyperfine fields at the Cd nucleus in NiO:Cd and MnO:Cd. Taking the overlap integrals listed in Table II and Table III we calculate in the same manner as above the hyperfine field at the impurity in MnO:Cd. Our new estimate for f_σ (Mn-O) listed in Table II is that value for which the ratio $[H(\text{MnO})/H(\text{NiO})]_{\text{calc}}$ of the calculated hyperfine fields is equal to the ratio of the experimentally observed ones. It is to be expected that this ratio can be calculated more reliably than the ratio $[H(\text{NiO})/H(\text{KNiF}_3)]_{\text{calc}}$ because the cadmium anion, that is, the Cd-O bond is the same in both materials. Our estimate f_σ(Mn-O) = 8.1% is considerably larger than the value f_σ = 1.47% deduced from a neutron-diffraction study.[28] It would be very difficult to understand that the hyperfine fields in NiO:Cd and MnO:Cd are almost identical, if we adopted the latter value for f_σ. However, spin-density parameters obtained by comparing supertransferred hyperfine fields might depend on the model used for the transfer of spin density, which makes it difficult to estimate an error limit.

In our previous Letter[1] we reported for f_σ (Mn-F) = 3.8% a value which was obtained by assuming the ratio of the f_σ 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. (5) this is only approximately true. Including the spin transfer through the 2*s* function of F^- and the charge transfer into the 5*s* orbital of Cd^{2+} we have reestimated this value in the same way as described above. However, since the hyperfine fields in $RbMnF_3$:Cd and $KNiF_3$:Cd are almost the same, our new estimate (Table II) is unchanged.

Because of the complicated electronic ground state of Co^{2+} in a predominantly octahedral crystal field, it is more difficult to deduce f_σ for $KCoF_3$:Cd and CoO:Cd. According to the theory of Abragam and Pryce,[29] the spin expectation value for the lowest Kramers doublet in a pure octahedral field is $\langle S\rangle = \frac{5}{6}$, that is $\langle S\rangle/S = \frac{5}{9}$. This value is changed by an axial component of the crystal field. As is well known, in the antiferromagnetic state, $KCoF_3$ and CoO distort tetragonally. Furthermore, an axial component of the crystal field might be caused by the neighboring Cd impurity. Because of the uncertainties connected with the factor $\langle S\rangle/S$ we do not estimate f_σ for the cobalt compounds. However, compared to $KNiF_3$ and NiO for which the ratio $\langle S\rangle/S$ is one except for a small correction due to the zero spin deviation, this factor is reduced in $KCoF_3$ and CoO because of the unquenched orbital angular momentum. As can be seen from Table I the hyperfine fields at the Cd impurity in these compounds are smaller than those in $KNiF_3$/Cd and NiO/Cd, respectively.

IV. CONCLUSIONS

The perturbed angular correlation of $^{111}Cd^m$ 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_σ(Ni-F), f_s (Ni-F), f_σ(Ni-O), f_s (Ni-O) known from NMR ($KNiF_3$) and ENDOR $[\text{Mg}(\text{Ni}^{2+})\ ^{17}\text{O}]$, 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 excitations into account. From the ratio of the hyperfine fields H(MnO)/H(NiO) a new estimate for the spin-density parameter f_σ(Mn-O) = 8.1% has been obtained, which is considerably larger than the value inferred from neutron diffraction.

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