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### Exchange Polarization Contribution to the Hyperfine Fields in $\text{ZnF}_2 : \text{Mn}$

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In calculations of the transferred hyperfine field at ligand-ion nuclei in transition-metal compounds, overlap and covalency effects are usually accounted for, but the exchange-core polarization of ligand closed electron shells due to the unpaired metal-ion orbitals are neglected. We have calculated this interaction for  $\text{ZnF}_2 : \text{Mn}$ , using the moment-perturbation technique and a model of free-ion orbitals distorted only by overlap. We find that the net contribution in this case is small because of an interesting cancellation of large individual terms. The hyperfine field at the  $\text{Mn}^{55}$  nucleus arises from exchange polarization of the  $s$  cores by the unpaired  $\text{Mn}^{++}$   $d$  orbitals. In the crystal, both the core  $s$  and valence  $d$  orbitals are distorted by overlap, and thus the hyperfine field at the  $\text{Mn}^{++}$  nucleus is changed from the free-ion value. The major overlap contribution is found to arise from the Pauli distortion of the  $\text{Mn}^{++}$   $s$ -core orbitals by surrounding ligand orbitals, and this effect is shown to decrease the magnitude of the free-ion value, in agreement with experiment.

#### I. INTRODUCTION

The transferred hyperfine field and the hyperfine field at paramagnetic-ion nuclei have been extensively used to study the electronic distribution of ionic crystals containing paramagnetic ions. In particular, attention has been focused on ionic crystals containing iron-group ions  $\text{ZnF}_2 : \text{Mn}$ ,  $\text{MnF}_2$ , and  $\text{KMnF}_3$ , to name a few. Several calculations<sup>1-13</sup> have been carried out for the transferred hyperfine constant (THC) of fluorine ligands.

The first such calculation<sup>2</sup> included only Pauli overlap polarization, where the unpaired spin of the paramagnetic ion overlaps the ligand orbitals of like spin. In effect this creates a net positive density at the ligand nuclei since the like-spin electrons on the  $\text{F}^-$  ions have their density squeezed inward and thus increased at the  $\text{F}^{19}$  nucleus relative to the unlike spin. This Pauli effect can be thought of as an overlap core polarization

(OCP) and results in a contribution to  $a_{\text{THC}}$  as given by the expression in Eq. (1) for an unpaired valence orbital on site  $i$  interacting with a paired-core orbital on site  $j$ :

$$a_{\text{OCP}} = \frac{8}{3}\pi(\mu/IS) \times \frac{1}{2} |\psi_{\text{val}}(R_j) - \langle \psi_{\text{val}} | \psi_{\text{core}} \rangle \psi_{\text{core}}(0)|^2, \quad (1)$$

where  $\mu$  is the nuclear magnetic moment of the nucleus. A comment should be made about the units to be used in this paper since different authors use a variety of units such as electron gauss, kG,  $\text{cm}^{-1}$ , and Mc/sec. In this paper we shall reference our values to the spin Hamiltonian  $\mathcal{H} = a I_z \langle S_z \rangle$  and will give values of  $a$  in units of field, electron gauss, by dividing  $a$  by  $g \mu_B$ . This description of  $a$  corresponds to most of the experimental values relevant to this study. The magnitude of  $a_{\text{THC}}$  at  $\text{F}^{19}$  nuclei from this effect alone is found to be only about 30% of experiment in the systems listed above.

Ideally, one would like to have wave functions for the crystal which would describe charge and spin densities accurately over all regions. Such wave functions would have to include covalency effects such as charge transfer and deformation of atomic orbitals as well as some correlation to account for many-body effects. While such wave functions are not currently available, several attempts to calculate good wave functions with flexible basis sets are in progress. On the other hand, there is a body of literature where departure of  $a_{\text{OCP}}$  from experiment is used to estimate the amount of charge transfer present. Such transfer effects result in a transfer on to  $\text{Mn}^{++}$  of ligand spin density unlike the  $\text{Mn}^{++}$  3d spin density, leaving behind a net positive density at the ligand nucleus, positive here being used for spin density of the same sign as the occupied  $\text{Mn}^{++}$  d orbitals. We shall denote this charge-transfer-polarization contribution as  $a_{\text{CTP}}$ .

However, it has long been realized<sup>1</sup> that it is possible for a third mechanism to make a significant contribution to  $a_{\text{THC}}$ , namely polarization of the ligand electrons through exchange with the unpaired electrons of the paramagnetic center. This effect may be termed exchange core polarization (ECP). The importance of this third mechanism has been dramatized recently by the experimental measurements<sup>14,15</sup> of sizable negative THC's, particularly for  $\text{Li}^+$ - and  $\text{F}^-$ -ion nuclei surrounding the  $V_K$  center in  $\text{LiF}$ . For those ions lying on the nodal plane of the  $\text{F}_2^-$  molecular ion,  $a_{\text{OCP}}$  is zero and  $a_{\text{CTP}}$  is either negligible or positive and could not explain the negative  $a_{\text{THC}}$ . However, as will be discussed later,  $a_{\text{ECP}}$  is capable of producing such a negative term. In effect, previous calculation in transition-ion compounds have been made under the assumption that this ECP contribution to the transferred hyperfine constant would be negligible. Of course uhf calculations in Refs. 9 and 10 automatically involve  $a_{\text{ECP}}$ , but the aim of that work was not to attain wave functions of sufficient accuracy at the fluorine nuclei to make quantitative statements about the importance of  $a_{\text{ECP}}$ . One of the two aims of this paper is to gain a quantitative understanding of the role ECP plays in transferred hyperfine interactions.

Also of interest both experimentally and theoretically is the hyperfine field at the  $\text{Mn}^{++}$ -ion nucleus. Here the situation is quite different from that for the  $\text{F}^-$  ion since  $a_{\text{Mn}^{++}}$  is not zero for the free ion as was the case for  $a_{\text{THC}}$ . Although the unpaired orbitals on  $\text{Mn}^{++}$  are d states and have no density at the nucleus, they can exchange-core polarize the paired s states yielding a finite contact interaction. For the free ion no experimental data are available, but theoretical calculations by

Watson and Freeman<sup>1</sup> yield a negative value for  $a_{\text{Mn}^{++}}$  that is larger in magnitude than the value observed experimentally for  $\text{Mn}^{++}$  in  $\text{ZnF}_2$ : Mn. Some decrease from the free-ion value could be explained by the charge transfer of negative fluorine spin density to the Mn 3d unoccupied down-spin state, in effect lessening the amount of unpaired d spin density on  $\text{Mn}^{++}$  and hence reducing the magnitude of  $a_{\text{Mn}^{++}}$ . In addition, it would be possible for transfer to the 4s state of spin one like the d orbitals, yielding a positive contribution. However, Šimanek has pointed out that in order to explain the large decrease in  $a_{\text{Mn}^{++}}$  observed for  $\text{Mn}^{++}$  in more covalent compounds that large transfer would be necessary, which would leave behind large THC's on the ligand opposite in sign to experiment. Instead, he proposes that nearby equal up- and down-spin transfer takes place in the unoccupied 4s orbitals on  $\text{Mn}^{++}$  and that ECP of this orbital which is large and positive for the Mn atom is the explanation of the decrease in magnitude of  $a_{\text{Mn}^{++}}$  in the solid state. However, without transfer there could also be a change from the free-ion value simply because of the influence of the ligand orbitals overlapping the  $\text{Mn}^{++}$  orbitals. This effect must be included if we are to judge the need for 4s charge transfer from comparison with experimental hyperfine constants. The second aim of this work is to gain quantitative understanding of  $a_{\text{Mn}^{++}}$ .

In Sec. II we outline the theory for calculation of  $a_{\text{THC}}$  and  $a_{\text{Mn}^{++}}$  we present our results and conclusions in Secs. III and IV, respectively.

## II. THEORY

In our calculation we have utilized the moment-perturbation (MP) technique<sup>16</sup> which handles the differences of up and down s-state densities at the nucleus as a perturbation. In previous calculations<sup>17</sup> it has compared quite closely to other perturbation calculations and in particular to results from Brueckner-Goldstone many-body perturbation technique<sup>18</sup> when many-body effects are unimportant, and has been utilized successfully to calculate Knight shifts in metals.<sup>16</sup> This method had previously been extended<sup>19</sup> to the case where the orbitals are nonorthogonal, such as for the THC calculations where  $\text{Mn}^{++}$  and  $\text{F}^-$  orbitals are non-orthogonal. For problems such as the calculation of  $a_{\text{ECP}}$  the perturbing Hamiltonian is composed of two parts, one representing the Fermi contact interaction and one the exchange potential:

$$\mathcal{H}_{\text{FC}} = \frac{8}{3}\pi \vec{\mu}_e \cdot \vec{\mu} \delta(\vec{r}) = \frac{8}{3}\pi g\mu_B g_N \mu_N \vec{I} \cdot \vec{S} \delta(\vec{r}),$$

$$\mathcal{H}_{\text{EX}} = - \sum_i \frac{\psi_{\text{val}}(i)}{\psi_{\text{core}}(i)} \int \psi_{\text{val}}(2) \frac{e^2}{r_{12}} \psi_{\text{core}}(2) d\tau_2, \quad (2)$$

where  $\mu_B$  and  $\mu_N$  are the Bohr and nuclear magnetons and  $g$  and  $g_N$  are the  $g$  factors of electron and nucleus, respectively.

Looking for terms in the total energy that are linear in the nuclear moment  $\mu$ , we could proceed in either of two ways. One way is for  $\mathcal{H}_{\text{EX}}$  to charge polarize the  $s$  cores which then have different  $s\uparrow$  and  $s\downarrow$  densities which have a finite interaction with  $\mathcal{H}_{\text{FC}}$ . However, this method is difficult to apply to solid-state problems since one must solve a multicentered differential equation to obtain  $\delta\psi_{\text{EX}}$  perturbed to first order in  $\mathcal{H}_{\text{EX}}$ . Alternatively, one could let  $\mathcal{H}_{\text{FC}}$  perturb the  $s$ -core states of the atom or ions in question and then carry out the exchange integral with the unpaired valence states using  $\mathcal{H}_{\text{EX}}$ . The advantage of this latter method (MP) is that one expects the first-order change in the wave function due to  $\mathcal{H}_{\text{FC}}(\delta\psi_N)$  to be reasonably independent of its outside environment; hence, solutions for the free ion can effectively be utilized for solid-state problems. In this approach we evaluate multicentered integrals involving  $\delta\psi_N$  rather than solve a multicentered differential equation. This method has already been applied to the calculation of  $a_{\text{ECP}}$  for  $\text{Li}^+$  and  $\text{F}^-$  ion nuclei surrounding  $V_K$  center in  $\text{LiF}$  and lying on the nodal plane of the  $\text{F}_2$  molecular ion<sup>20</sup> where, as was mentioned in Sec. I,  $a_{\text{OCP}}$  and  $a_{\text{CTP}}$  could not explain the experimentally observed negative sign of  $a_{\text{THC}}$ . From calculation<sup>20</sup> it was shown that  $a_{\text{ECP}}$  could explain the sign and magnitude of  $a_{\text{THC}}$  and further showed that  $a_{\text{ECP}}$  could make a sizable contribution to  $a_{\text{THC}}$ ; to neglect it in general is not justified.

We shall consider the  $\text{ZnF}_2:\text{Mn}$  system where experimental data are available<sup>21</sup> and where we need consider only a pair-wise interaction between  $\text{Mn}^{++}$  and  $\text{F}^-$  ions. We neglected the ligand-ligand interaction, which should not alter our conclusion about the importance of  $a_{\text{ECP}}$  since its main contribution arises from the  $\text{Mn}^{++}$  and  $\text{F}^-$  exchange interaction. The structure of  $\text{ZnF}_2:\text{Mn}$  is rutile and the local symmetry around  $\text{Mn}^{++}$  is distorted from cubic with two  $\text{F}^-$  ions being at a distance slightly different from the other four. As will be seen, it will not alter any of our conclusions if we consider the  $\text{F}^-$  ions all to be at an intermediate distance of  $3.85 a_0$ . This makes our situation similar to  $\text{KMnF}_3$  and  $\text{MnF}_2$  and the conclusion reached here for  $\text{ZnF}_2:\text{Mn}$  should also hold for the other systems. Our model for the crystal wave function is one in which it is assumed that the only distortion from their free-ion form is due to overlap with their neighbors. The calculation for  $a_{\text{ECP}}$  is the type I situation in Ref. 19 and we can easily write down its expression in Eq. (3). In evaluating Eq. (3) we retain terms which are second order in

overlap and neglect higher orders. Here an integral such as

$$\langle \text{Mn}(1) \text{F}(1) | e^2/r_{12} | \text{F}(2) \text{Mn}(2) \rangle$$

is counted as two orders in overlap. (Note that in all formulas and tables we shall denote  $\text{Mn}^{++}$  and  $\text{F}^-$  merely by the symbols Mn and F, respectively.) We obtain

$$\begin{aligned} a_{\text{ECP}} = & -2A \\ & \times \sum_{i=1}^5 \sum_{j=1}^2 \langle \chi_{di}(1) \delta \chi_{sj}(1) | (e^2/r_{12}) | \chi_{sj}(1) \chi_{di}(2) \rangle, \\ \chi_{s1} = & N_{s1} [F_{1s} \\ & - \langle F_{1s} | \text{Mn}_{3s} \rangle \text{Mn}_{3s} - \langle F_{1s} | \text{Mn}_{3p_0} \rangle \text{Mn}_{3p_0}], \\ \chi_{s2} = & N_{s2} [F_{2s} \\ & - \langle F_{2s} | \text{Mn}_{3s} \rangle \text{Mn}_{3s} - \langle F_{2s} | \text{Mn}_{3p_0} \rangle \text{Mn}_{3p_0}], \\ \chi_{d1} = & N_{d1} [\text{Mn}_{3d_1} - \langle \text{Mn}_{3d_1} | F_{2p_1} \rangle F_{2p_1}], \\ \chi_{d2} = & N_{d2} [\text{Mn}_{3d_{-1}} - \langle \text{Mn}_{3d_{-1}} | F_{2p_{-1}} \rangle F_{2p_{-1}}], \\ \chi_{d3} = & \text{Mn}_{3d_2}, \\ \chi_{d4} = & \text{Mn}_{3d_{-2}}, \\ \chi_{d5} = & N_{d5} [\text{Mn}_{3d_0} - \langle \text{Mn}_{3d_0} | F_{1s} \rangle F_{1s} \\ & - \langle \text{Mn}_{3d_0} | F_{2s} \rangle F_{2s} - \langle \text{Mn}_{3d_0} | F_{2p_0} \rangle F_{2p_0}], \\ \delta \chi_{s1} = & \delta F_{1s} \\ & - F_{1s} | \text{Mn}_{3s} \rangle \text{Mn}_{3s} - \langle F_{1s} | \text{Mn}_{3p} \rangle \text{Mn}_{3p}, \\ \delta \chi_{s2} = & \delta F_{2s} \\ & - \langle F_{2s} | \text{Mn}_{3s} \rangle \text{Mn}_{3s} - \langle F_{2s} | \text{Mn}_{3p} \rangle \text{Mn}_{3p}, \\ A = & \frac{8}{3} \pi \mu / IS \times \frac{1}{2} (2m) / a_0. \end{aligned} \quad (3)$$

The  $\delta\chi$  are defined as in Ref. 16 divided by  $4\pi$ . The expression for  $a_{\text{Mn}^{++}}$  is similar but like the type II situation in Ref. 19.

### III. RESULTS AND DISCUSSION

Before proceeding to the calculation of  $a_{\text{ECP}}$  we shall present the results of  $a_{\text{OCP}}$  which had previously been calculated,<sup>2</sup> including only the  $\text{F}_{2s}^-$  orbital. However, as has been pointed out,<sup>3</sup> a large contribution comes from including  $\text{F}_{1s}^-$ . Using Eq. (1) and the orthogonalized wave function in Eq. (3), we obtain the expression

$$\begin{aligned} a_{\text{OCP}} = & \frac{8}{3} \pi \mu / IS \\ & \times \frac{1}{2} | \text{Mn}(r_F) - S_{\text{F}_{1s}}^{\text{Mn}} F_{1s}(0) - S_{\text{F}_{2s}}^{\text{Mn}} F_{2s}(0) |^2, \end{aligned} \quad (4)$$

where  $S_a^b$  is the overlap between orbitals  $a$  and  $b$ . Contributions of the various terms are listed in Table I. It can be seen that we obtain almost the same result as was found previously<sup>3</sup> for  $\text{KMnF}_3$ . The result of  $a_{\text{OCP}} = 6.4$  electron gauss is only about 35% of experiment,<sup>21</sup> but if  $\text{F}_{2s}^-$  is not included, the result is 70% of experiment, as was found in

TABLE I. Contributions to  $a_{\text{OCP}}$ .

Term	Value
1 $  \text{Mn}_{3d}(\tilde{r}_F)  ^2$	0.000 067
2 $  \langle F_{1s}   \text{Mn}_{3d_0} \rangle F_{1s}(0)  ^2$	0.005 335
3 $  \langle F_{2s}   \text{Mn}_{3d_0} \rangle F_{2s}(0)  ^2$	0.046 734
4 $2 \langle F_{1s}   \text{Mn}_{3d_0} \rangle \langle F_{2s}   \text{Mn}_{3d_0} \rangle F_{2s}(0) F_{1s}(0)$	-0.031 520
5 $-2 \langle F_{1s}   \text{Mn}_{3d_0} \rangle F_{1s}(0) \text{Mn}_{3d_0}(\tilde{r}_F)$	-0.001 180
6 $-2 \langle F_{2s}   \text{Mn}_{3d_0} \rangle F_{2s}(0) \text{Mn}_{3d_0}(\tilde{r}_F)$	0.003 540
Total of terms 1-6	0.022 976
$a_{\text{OCP}}$ Total (electron gauss)	6.4

Ref. 2. Thus, a proper treatment of  $a_{\text{OCP}}$  rules out the possibility that it alone is able to explain the experimentally observed THC.

We now turn to the evaluation of  $a_{\text{ECP}}$  as given in Eq. (3). The equation to determine the MP wave functions for  $F^-$  and  $\text{Mn}^{++}$  s orbitals was solved using Eq. (17) of Ref. 22, the local approximation for the potential as was done in Ref. 16, and a non-iterative approach to solve this integral differential equation as described in Ref. 22.  $F^-$  and  $\text{Mn}^{++}$  wave functions are due to Clementi,<sup>23</sup> and Löwdin's  $\alpha$ -function technique<sup>24</sup> was used to handle the multicentered integrals in Eq. (3). A discussion of the approximations made here is presented by Duff<sup>20</sup> and it appears that they will not alter our results by more than 10% and thus will not alter any conclusions that we are attempting to arrive at in this work.

The leading individual contributions to  $a_{\text{ECP}}$  that we have obtained from Eq. (3) are presented in

Table II, in particular for the  $\text{Mn}_{3d_0}^{++}$  orbital and the case of  $F^-$ - $\text{Mn}^{++}$  pair oriented along the  $z$  axis. The most interesting feature of these results is that although the individual terms are quite large because of cancellation, the net result is quite small. Term (a) by itself would contribute about 10  $g$  the amount needed to reach agreement with experiment. It is possible to associate different physical effects with the terms in Table II. Consider first the effects that arise from the direct ECP of the ligands by the unpaired  $\text{Mn}^{++}$  3d orbitals and the unorthogonalized  $F_{2s}^-$  core, namely terms a-d in Table II, which can be written as

$$a_{\text{ECP}} = -2A \langle (\text{Mn}_d - S_{F_{2s}}^{\text{Mn}} F_{2s}) \times \delta F_{2s} | e^2/r_{12} | F_{2s} (\text{Mn}_d - S_{F_{2s}}^{\text{Mn}} F_{2s}) \rangle. \quad (5)$$

This expression can be compared to Eq. (4) with the  $F_{1s}^-$  absent:

$$a_{\text{OCP}} = \frac{8}{3} \pi \mu / IS \times \frac{1}{2} | \text{Mn}_d(r_F) - S_{F_{2s}}^{\text{Mn}} F_{2s}(0) |^2. \quad (6)$$

In Eq. (6) almost the entire contribution comes from  $S^2 | F_{2s}(0) |^2$ , that is, not the direct 3d density at the  $F^{19}$  nucleus but its effect on the  $F_{2s}^-$  orbital through Pauli overlap distortion. In contrast, in Eq. (5) there is a balance between the direct-exchange polarization, by the 3d  $\text{Mn}^{++}$  electrons, which is negative and the exchange polarization, modified by overlap effects, which is predominately positive. Further comments about this point will be presented in Sec. IV. Terms e-g are direct ECP mediated through overlap with the  $F_{2p}^-$  electrons.

TABLE II. Contributions to  $a_{\text{ECP}}$  for  $F^-$  in  $\text{ZnF}_2:\text{Mn}$ .

Term	$\langle (1)(1)   (e^2/r_{12})   (2)(2) \rangle$	Value/A
a	$-2 \langle \text{Mn}_{3d} \delta F_{2s}   F_{2s} \text{Mn}_{3d} \rangle$	-0.017 872
b	$+2 \langle \text{Mn}_{3d}   F_{2s} \rangle \langle \text{Mn}_{3d} \delta F_{2s}   F_{2s} F_{2s} \rangle$	0.010 680
c	$+2 \langle \text{Mn}_{3d}   F_{2s} \rangle \langle F_{2s} \delta F_{2s}   F_{2s} \text{Mn}_{3d} \rangle$	-0.001 988
d	$-2   \langle \text{Mn}_{3d}   F_{2s} \rangle  ^2 \langle F_{2s} \delta F_{2s}   F_{2s} F_{2s} \rangle$	0.004 976
e	$\langle \text{Mn}_{3d}   F_{2p} \rangle \langle \text{Mn}_{3d} \delta F_{2s}   F_{2s} F_{2p} \rangle$	0.002 832
f	$+2 \langle \text{Mn}_{3d}   F_{2p} \rangle \langle F_{2p} \delta F_{2s}   F_{2s} \text{Mn}_{3d} \rangle$	0.000 712
g	$-2 \langle \text{Mn}_{3d}   F_{2p} \rangle \langle \text{Mn}_{3d}   F_{2p} \rangle \langle F_{2p} \delta F_{2s}   F_{2s} F_{2p} \rangle$	0.000 848
h	$-2 \langle \delta F_{2s}   \text{Mn}_{3s} \rangle \langle F_{2s}   \text{Mn}_{3s} \rangle \langle \text{Mn}_{3d} \text{Mn}_{3s}   \text{Mn}_{3s} \text{Mn}_{3d} \rangle$	-0.000 448
i	$-2 \langle \delta F_{2s}   \text{Mn}_{3p} \rangle \langle F_{2s}   \text{Mn}_{3p} \rangle \langle \text{Mn}_{3d} \text{Mn}_{3p}   \text{Mn}_{3p} \text{Mn}_{3d} \rangle$	-0.001 546
j	$+2 \langle F_{2s}   \text{Mn}_{3s} \rangle \langle \text{Mn}_{3d} \delta F_{2s}   \text{Mn}_{3s} \text{Mn}_{3d} \rangle$	0.000 558
k	$+2 \langle \delta F_{2s}   \text{Mn}_{3s} \rangle \langle \text{Mn}_{3d} \text{Mn}_{3s}   F_{2s} \text{Mn}_{3d} \rangle$	0.000 744
l	$+2 \langle F_{2s}   \text{Mn}_{3p} \rangle \langle \text{Mn}_{3d} \delta F_{2s}   \text{Mn}_{3p} \text{Mn}_{3d} \rangle$	0.001 590
m	$+2 \langle \delta F_{2s}   \text{Mn}_{3p} \rangle \langle \text{Mn}_{3d} \text{Mn}_{3p}   F_{2s} \text{Mn}_{3d} \rangle$	0.001 990
	Total these terms $\text{Mn}_{3d_0}$	0.003 076
	Sum of all other $\text{Mn}_{3d_0}$	0.000 228
	Total $\text{Mn}_{3d_0}$	0.003 304
	Total all other $\text{Mn}_{3d \pm 1}$	-0.002 044
	$\text{Mn}_{3d \pm 2}$	0.001 260
	$a_{\text{ECP}}$ Total (electron gauss)	~ 0

Next we consider indirect ECP where the  $\text{Mn}^{++}$   $3d$  orbitals polarize the  $\text{Mn}^{++}$ -filled  $3s$  and  $3p$  cores which in turn overlap the ligand  $2s$  core unequally, creating an unbalancing of the  $2s$  density at the  $\text{F}^{19}$  nucleus (terms h-i). There are also terms which are a cross between the direct and indirect ECP, namely j-m on Table II, and we prefer to group them with the indirect ECP since they would vanish if the filled core orbitals on  $\text{Mn}^{++}$  and  $\text{F}^-$  did not overlap. Again it can be seen that among those indirect terms there is cancellation and that they are individually about an order of magnitude smaller than the direct terms.

The contribution from  $\text{Mn}_{3d+1}^{++}$  and  $\text{Mn}_{3d+2}^{++}$  orbitals have similar contributing terms, except that their overlap integral with  $\text{F}^-$   $s$  core orbitals is zero and the direct ECP is dominated by the negative terms. When all the terms are added together the result is small.

The situation for  $a_{\text{Mn}^{++}}$  is quite different since we are looking for a change to an already large field. In Table III we present the free-ion values calculated by the MP method. The result is  $-123$  electron gauss, compared to Watson and Freeman's uhf value<sup>1</sup> of  $-106$  electron gauss. In Table IV we give a few leading terms due to two-center ECP effects for  $\text{ZnF}_2:\text{Mn}$ . Since there are six  $\text{F}^-$  ligands surrounding  $\text{Mn}^{++}$ , we multiply this contribution by 6. As can be seen from Table IV there is one type of term which contributes significantly, namely those that involve the effect of the  $\text{F}_{2s}$  and  $\text{F}_{2p}$  cores on  $\text{Mn}^{++}$   $3s$  core through orthogonalization. In effect, this places density outside the  $3d$  unpaired electron which appears to then attract more like-spin density inwards. The net contribution of 29 is positive and reduces the free-ion value of  $-123$  to  $-94$ , which is in the proper direction and of sufficient magnitude to agree with the experimental value<sup>21</sup>  $-97.1$  all in electron gauss, which are the units used in Ref. 21. We are able to explain the experimentally observed decrease without any other mechanism such as  $4s$  charge transfer. In some measure this is in opposition to Šimanek's recent calculation in which he used a charge transfer to the  $4s$  state and subsequent one-center ECP of this transferred  $4s$  density. Re-

TABLE III. Contributions to  $a_{\text{ECP}}\text{Mn}^{++}$  free ion referenced to spin Hamiltonian  $\mathcal{H} = a\vec{I} \cdot \vec{S}$ .

	$a_{\text{ECP}}$ ( $\text{Mn}^{++}$ free ion)
1s	0
2s	-102
3s	-21
$a_{\text{ECP}}$ (free ion)	
Total (electron gauss)	-123

TABLE IV. Contribution to  $a_{\text{Mn}^{++}}$  in  $\text{ZnF}_2:\text{Mn}$ .

Term $\langle (1)(1)   (e^2/r_{12})   (2)(2) \rangle$	Value/A
$\langle \text{Mn}_{3s}   \text{F}_{2p} \rangle \langle \text{Mn}_{3d_0} \delta \text{Mn}_{3s}    \text{F}_{2p} \text{Mn}_{3d_0} \rangle$	0.003 258
$\langle \delta \text{Mn}_{3s}   \text{F}_{2p} \rangle \langle \text{Mn}_{3d_0} \text{F}_{2p}    \text{Mn}_{3s} \text{Mn}_{3d_0} \rangle$	0.008 600
$\langle \delta \text{Mn}_{3s}   \text{F}_{2s} \rangle \langle \text{Mn}_{3d_0} \text{F}_{2s}    \text{Mn}_{3s} \text{Mn}_{3d_0} \rangle$	0.000 866
$\langle \text{Mn}_{3s}   \text{F}_{2s} \rangle \langle \text{Mn}_{3d_0} \delta \text{Mn}_{3s}    \text{F}_{2s} \text{Mn}_{3d_0} \rangle$	0.000 340
Sum of above terms	0.013 064
Sum of all other terms with $\text{Mn}_{3d_0}$	0.003 272
Total from $\text{Mn}_{3d_0}$	0.016 340
Sum of all terms from $\text{Mn}_{3d+1}$ and $\text{Mn}_{3d_0}$	0.019 712
Total 3s	0.036 052
Total 2s	- 0.005 808
Total 1s	0
Total for one Mn-F pair	0.030 144
Total for Mn-F cluster	0.180 864
$a_{\text{Mn}}$ (electron gauss) from ECP effects	29
$a_{\text{Mn}}$ including free-ion value	- 94
$a_{\text{Mn}}$ (expt)	- 97.1

cent configuration calculation by Hubbard *et al.*<sup>8</sup> would seem to be more in line with our calculation to explain the reduced magnitude of  $a_{\text{Mn}^{++}}$ . For more covalent situations such as  $\text{ZnS}:\text{Mn}$ , Šimanek proposed that quite sizable  $4s$  transfer was needed, but for these more diffused systems the overlap is also large and hence we would expect a larger reduction of ECP at  $\text{Mn}^{++}$  without  $4s$  transfer. It should be pointed out that overlap distortion does bring into play charge density in the same vicinity as would  $4s$  charge transfer but is present with or without  $4s$  transfer. First-principle calculations of  $4s$  transfer or ECP in these systems are needed to answer the question of whether there really is sizable transfer.

#### IV. CONCLUSIONS

Two basic conclusions can be reached from this study. For an ionic model distorted only by overlap, exchange polarization effects do not contribute significantly to the transferred hyperfine field at ligand  $\text{F}^-$  ions in  $\text{ZnF}_2:\text{Mn}$ , but do for the hyperfine field at  $\text{Mn}^{++}$  nuclei where exchange polarization contributions are of proper sign and sufficient magnitude to explain the experimentally observed reduction in the field relative to the free ion. This latter conclusion removes the necessity of  $4s$  charge transfer in explanation of  $a_{\text{Mn}^{++}}$ . For the transferred hyperfine field, although individual contributions are large, cancellation leads to a small result and since overlap contributions to  $a_{\text{THC}}$  for  $\text{F}^-$  are only about 35% of experiment, it appears that further covalency effects must contribute significantly. It should be pointed out that other properties such as temperature dependence

which depend on 4s transfer will also be effected by this exchange mechanism.

We can also make some more general comments about the role of ECP in ionic crystals with paramagnetic ions or color centers by combining the results of this calculation with two previous ones, the transferred hyperfine interaction at  $\text{Li}^+$  nuclei adjacent to an  $\text{F}^-$  center in  $\text{LiF}$  and  $\text{Li}^+$  and  $\text{F}^-$  nuclei lying on the nodal plane of the  $V_K$  center in  $\text{LiF}$ . In these systems there is a variance in the overlap integral between the unpaired valence orbital and the ligand core s orbital; zero for  $\text{Li}^+$  and  $\text{F}^-$  ions on the nodal plane of the  $\text{F}_2^-$  molecular ion in  $\text{LiF}$ , 0.07 for  $\text{ZnF}_2$ :Mn and 0.10 for  $\text{Li}^+$  ion adjacent to the F center in  $\text{LiF}$ . The value of  $a_{\text{ECP}}$  in these systems is negative, nearly zero, and positive, respectively. Thus, it appears with increasing overlap  $a_{\text{ECP}}$  becomes more positive. Physically, this may roughly be looked at in the following way for two centers with overlapping charge distribution: When the overlap is small or zero, exchange acting like an attractive potential pulls charge density into the region of the unpaired spin and away from the nucleus where  $a_{\text{THC}}$  is being measured. As the overlap between the distribution increases the unpaired electrons get more inside the neighboring charge distribution and also begin to attract charge density towards the nucleus where  $a_{\text{THC}}$  is being calculated. Since the density in the second mechanism is much closer to the nucleus than for the first, less unpaired density is needed for a sizable contribution to  $a_{\text{THC}}$ . There is cancellation between the two mechanisms and the sign of  $a_{\text{THC}}$  can be negative or positive depending on whether the first or second effect is more im-

portant. For intermediate cases  $a_{\text{THC}}$  is small.

Of course it should be pointed out that as the overlap increases, so might various covalency effects which make the simple model of distortion only by overlap quite inadequate. For example the orbitals in the crystal may contract or expand from their free-ion form and charge-transfer covalency effects may become important. There are two ways that covalency effects could be important: directly as from charge transfer, and indirectly, where deformation of the orbitals could change the value of  $a_{\text{ECP}}$ . It should be pointed out that when detailed restricted Hartree-Fock self-consistent wave functions are available for the crystal we can proceed in the same manner or as was done in this paper, i.e., find MP orbitals for the new charge density and then calculate  $a_{\text{ECP}}$ . This allows an assessment of the importance of  $a_{\text{ECP}}$  by perturbation techniques handling only the difference of up and down s-state densities rather than subtracting them as is done in unrestricted Hartree-Fock calculations.

One further point should be mentioned concerning  $a_{\text{F}^-}$ . In the treatment carried out here we have neglected higher-order terms in  $\mathcal{H}_{\text{EX}}$  such as  $\mathcal{H}_{\text{EX}}^2 \mathcal{H}_{\text{FE}}$ . Although expected to be smaller than  $\mathcal{H}_{\text{EX}} \mathcal{H}_{\text{FC}}$  for individual terms, it is not clear that the total will be smaller due to the severe cancellations among terms that we found in calculating  $a_{\text{F}^-}$ .  $\mathcal{H}_{\text{EX}}^2 \mathcal{H}_{\text{FC}}$  does not bring about another order in two centeredness, but merely adds a one-center  $\mathcal{H}_{\text{EX}}$  interaction; for example,  $\text{Mn}_{3d}$  exchange polarizes  $\text{F}_{2p}$ , which in turn exchange polarizes  $\text{F}_{2s}$  on the same center. Our present method would have to be reformulated to include such effects.

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PHYSICAL REVIEW B

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## Hyperfine Structure in Trivalent Plutonium

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The hyperfine structure constants of  $\text{Pu}^{3+}$  in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  are analyzed and the values  $\langle 1/r^3 \rangle = 7.57 \pm 0.57$  a.u. and  $a_{\text{Pu}^{3+}} = -(556 \pm 42) (g_J - 1) (\mu_N/I)$  Mc/sec are derived. Relativistic Dirac-Slater and Dirac-Fock wave functions give a value for  $\langle 1/r^3 \rangle$  about 9% lower than the empirical value. The core-polarization effect in the actinide ion  $\text{Pu}^{3+}$  is much larger than in the lanthanide series.

### I. INTRODUCTION

Values of the nuclear dipole moment of  $^{239}\text{Pu}$  derived from different types of measurements varied widely when the data were first analyzed. Subsequent analyses showed these results could be brought into agreement by a complete theoretical treatment including intermediate coupling and core-polarization effects.<sup>1</sup> Attempts to explain the sign of the core-polarization term with basis wave functions obtained from the central-field model of atomic structure proved inadequate until admixtures of continuum states were included.<sup>1</sup> Unfortunately, this type of calculation is very difficult. Exchange-polarized Hartree-Fock calculations were able to account for the sign and approximate magnitude of core-polarization effects<sup>2</sup> in the lanthanide series.

The electron-paramagnetic-resonance spectra of  $\text{Pu}^{3+}$ ,  $5f^5$ , have recently been measured in cubic symmetry sites in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ . The Zeeman-splitting factors ( $g$  values) have been interpreted by calculating the crystalline field mixing of the first excited  $J = \frac{7}{2}$  state with the ground  $J = \frac{5}{2}$  state.<sup>3</sup> In this paper we analyze the hfs data for  $\text{Pu}^{3+}$  in a similar manner, and use the known nuclear magnetic moment<sup>4</sup> of  $^{239}\text{Pu}$  to derive values for the core-polarization effect and  $\langle 1/r^3 \rangle$ . The latter quantity is compared with various theoretical calculations.

### II. THEORY AND RESULTS

#### A. Theoretical Summary

The nonrelativistic hyperfine Hamiltonian may be written as

$$\mathcal{H} = (2\beta\beta_N\mu_N/I) \left[ \sum_i (\vec{N}_i \cdot \vec{I}/r_i^3) + \frac{1}{3} 8\pi \sum_i \delta(\vec{r}_i) \vec{s}_i \cdot \vec{I} \right], \quad (1)$$

where  $\beta$  and  $\beta_N$  are the Bohr magneton and the nuclear magneton, respectively,  $\mu_N$  is the nuclear moment,  $I$  is the nuclear spin,  $\vec{r}_i$  is the radius vector for the  $i$ th electron, and  $\delta(\vec{r}_i)$  is the Dirac  $\delta$  function which is nonzero only for  $s$  electrons. The operator  $\vec{N}_i$  for the  $i$ th electron is written in terms of tensor operators as

$$\vec{N}_i = \vec{L}_i - (10)^{1/2} (\vec{S}^{(1)} \vec{C}^{(2)})^{(1)}_i, \quad (2)$$

where  $\vec{L}_i$  and  $\vec{S}_i$  are the orbital and spin angular momentum vectors and  $\vec{C}^{(2)}$  is a second-rank tensor.<sup>5</sup> The operator  $\vec{N}_i$  has nonzero matrix elements only for electrons with  $l > 0$ . In order to account for the effect of core polarization which produces a net unpairing of  $s$  electrons, the second term is included in Eq. (1). The angular transformation properties of this term are proportional to the operator  $\vec{S}_i$ . Relativistic effects also transform as  $\vec{S}_i$  and are not distinguishable from core polarization in our present experiments.

For convenience of calculation, we follow the procedure of Bordarier *et al.*,<sup>6</sup> and introduce the coupled double-tensor operator  $\vec{W}^{(u,k)K}$ . For a configuration of equivalent electrons,  $l^N$ , the hyperfine operators are defined as

$$\begin{aligned} \vec{I} &= \left[ \frac{1}{3} 2l(l+1)(2l+1) \right]^{1/2} \vec{W}^{(01)1}, \\ -10^{1/2} (\vec{S}^{(1)} \vec{C}^{(2)})^{(1)} &= \left( \frac{l(l+1)(2l+1)}{(2l-1)(2l+3)} \right)^{1/2} \vec{W}^{(12)1}, \\ \vec{S} &= \left[ \frac{1}{2} (2l+1) \right]^{1/2} \vec{W}^{(10)1}. \end{aligned} \quad (3)$$