distortion, dipolar fields, and especially the anisotropy of the Fe-R exchange interactions. These last terms are probably also responsible for the existence of the transition regions.

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Orbital Contributions to the Transferred Hyperfine Fields in Rare-Earth Compounds

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Magnetic hyperfine fields acting on the nuclei of diamagnetic atoms in rare-earth intermetallic compounds are generally assumed to follow a form $H_{hf} = H_s (g_J - 1) \langle J_z \rangle$. However, such an expression is inadequate to describe the detailed dependence of the transferred hyperfine fields as the rare-earth ion is changed. It is shown that an expression based on a Hamiltonian which includes orbital contributions to the hyperfine field can describe the available data on several series of rare-earth compounds. This dependence has the form $H_{hf} = [(g_J - 1)H_{01} + (2 - g_J)H_{10} + c_n H_{21}] \langle J_z \rangle$, where the c_n are appropriate rare-earth reduced matrix elements. By fitting the extant data to this expression, we find that the orbital contributions H_{10} and H_{21} are appreciable. The general form of this expression is found to be valid for a variety of mechanisms which produce transferred and supertransferred hyperfine fields.

I. INTRODUCTION

The magnetic hyperfine field acting on the nuclei of diamagnetic atoms in rare-earth intermetallic compounds is generally considered to be a result of the s-f exchange interaction between conduction electrons and the rare-earth atoms. This produces a conduction-electron polarization which causes a hyperfine field on neighboring atoms directly through the contact interaction and indirectly through core polarization. Since both of these contributions are proportional to the conduction-electron polarization, measurements of the hyperfine fields have frequently been used in attempts to obtain information concerning the s-f interaction. In the most common approach, this interaction is written[1]

$$\mathcal{H}_{sf} = -2\Gamma_{sf}(g_J - 1)\vec{J} \cdot \vec{s}_{cond}, \tag{1}$$

where Γ_{sf} is an exchange coupling parameter, g_J is the Landé g factor for a rare-earth ion with total angular momentum J, and $\vec{s}_{cond}$ is the conduction-electron spin. In a series of isostructural compounds in which the rare-earth atom is changed, the resulting conduction-electron polarization produces a hyperfine field H_{hf} at the nuclei of neighboring atoms which should vary with the rare-earth component according to

$$H_{\text{hf}} = H_s(g_J - 1)\langle J_z \rangle , \qquad (2)$$

where H_s will depend on the conduction-electron susceptibility as well as the electronic structure of the diamagnetic atom.

This relation has been used a number of times in discussions of hyperfine fields obtained from Knight-shift,[2] angular-correlation,[3] and Mössbauer-effect[4-6] studies. While the rough dependence of H_{hf} on the rare-earth atom is obtained this way, it is not possible to explain the detailed behavior of the experimental results. Figure 1 shows data obtained by Knight-shift measurements[2] on ^{31}P for the series of compounds RP (R = rare earth). The dashed line shows the behavior of Eq. (2), where we have taken $\langle J_z \rangle = J$ at magnetic saturation. The degree of discrepancy between the expected behavior and the experimental results is typical for a number of other systems as well. Inclusion of crystal field effects, which generally tend to reduce $\langle J_z \rangle$, improves the fit somewhat for the heavy rare earths; however, it increases the discrepancy for most of the light rare earths. In no case does it provide a satisfactory resolution of the problem.

There have been some attempts to parametrize the data in other ways[4,5]; however, no widespread improvement has been obtained. It has been observed that similar deviations from the predictions of Eq. (1) occur for a wide range of other phenomena.[7] One can imagine a number of mechanisms which may cause changes from the simple dependence of Eq. (1). The effects of interband mixing between conduction and local-moment electron orbitals has been frequently discussed.[8-10] The result of such a mixing is to cause the effective exchange parameter to vary as the rare-earth ion is changed, and calculations indicate that this can account for discrepancies similar to those discussed here.[8,9] In the present work we wish to point out a separate effect which should in principle be included when considering these complex phenomena. We will consider effects such as interband mixing to be small by assuming a constant Γ_{sf} across the rare-earth series. One should realize, however, that this is done for the sake of simplicity and emphasis, and does not imply that such effects are truly negligible.

In this paper we consider orbital contributions to the transferred hyperfine coupling between a rare-earth ion and the nuclear spin of a neighboring ion. In general we find isotropic and anisotropic, linear and higher-degree contributions to the hyperfine field at the neighboring site due to the rare-earth ions. In light of the limited available data, we then consider the linear isotropic contributions for a discussion of the data. It is found that the orbital contributions to the hyperfine field are capable of

explaining the variations of these fields in rare-earth compounds as the rare-earth ion is changed.

II. THEORY

In analyzing the experimental data on a variety of physical properties, modifications of Eq. (1) have been found to occur when the anisotropy of the s-f exchange interaction is fully accounted for.[11-14] To determine the corrections to Eq. (2) associated with these modifications, we consider the indirect coupling of the rare-earth $4f$ electrons and the nuclear spin of a neighboring anion. We explicitly consider the following process: The s-f exchange interaction polarizes the conduction electrons and these electrons in turn produce the hyperfine field at a neighboring site. As we will discuss later, the form of the coupling derived using this process applies equally well to transferred and supertransferred hyperfine fields due to other processes.

Corrections to Eqs. (1) and (2) will be significant if the conduction electrons have some orbital degeneracy. The simplest wave function which is orbitally degenerate is of the form

$$\psi_{\vec{k}jm}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \psi_{nlsjm}(\vec{r}) , \qquad (3)$$

where

$$\psi_{nlsjm}(\vec{r}+\vec{R}) = \psi_{nlsjm}(\vec{r}) .$$

The translation $\vec{R}$ is by an integral number of lattice spacings. The wave function $\psi_{nlsjm}(\vec{r})$ resembles the wave function for the hydrogen atom. When the origin of this function is placed at a rare-earth site, the variables j and m only label the conduction-electron wave function at the anion site; they do not represent the total angular momentum at this site. We have written the above function in an $|lsjm\rangle$ representation. When the conduction electrons are in spin-orbit coupled states, we consider only one j manifold; if there is negligible spin-orbit coupling we consider all j manifolds arising from an (l, s) term to be degenerate. The electrons on the magnetic rare-earth ion are described by an atomic wave function of orbital angular momentum L and spin S:

$$\varphi = \psi_{NL M_L SM_S} .$$

By confining ourselves to single-pair interactions between the localized and itinerant electrons, the "s-f" exchange interaction is written as[12,15]

$$\mathcal{H}_{sf} = f(\vec{L}; \vec{k}jm, \vec{k}'j'm)(\tfrac{1}{2}\alpha + 2\beta\vec{S}\cdot\vec{s})$$

$$= \sum_{pK} A_{pK}(kj, k'j')[U^{[p]}(L) \times U^{[p]}(\hat{r})]^{[0]}$$

$$\times [S^{[K]} \times s^{[K]}]^{[0]} , \qquad (4)$$

where

$$A_{pK} = (\tfrac{1}{2}\alpha\delta_{K0} + 2\beta\delta_{K1})A^{(p)}(NL, kj; NL, k'j') .$$

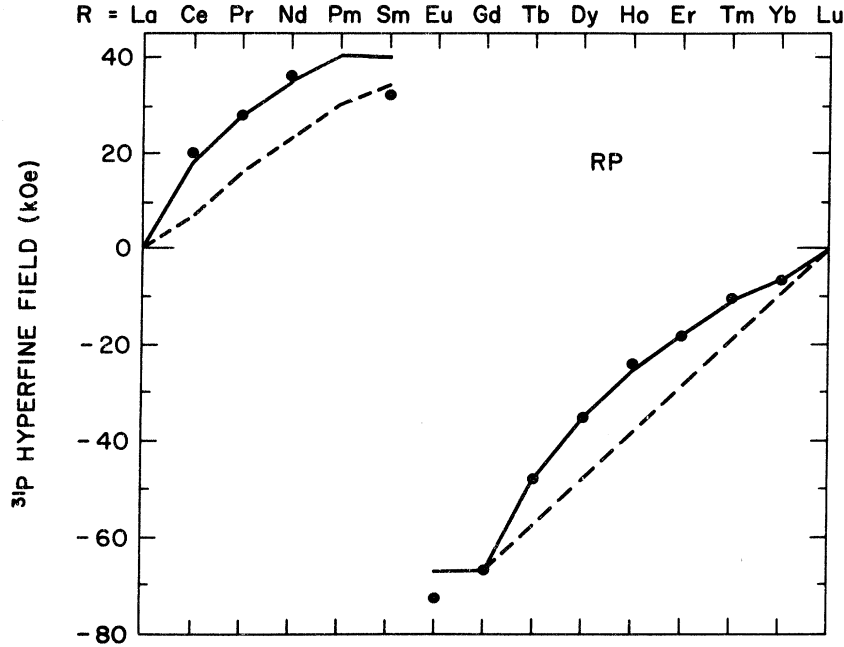These exchange parameters are related to the Γ_{pK}

FIG. 1. Comparison of experimental and calculated hyperfine fields for the compounds RP. Experimental points (solid circles) are obtained by Knight-shift measurements on ^{31}P (Ref. 2). Calculated curves are for Eq. (2) (dashed line) with $H_s = -19$ kOe and Eq. (12) (solid line) using parameters given in Table III. Since insufficient data are available to correct for crystal field interactions, we have taken $\mu_{\text{expt}} = \mu_{\text{FI}}$.

previously defined[13,14] as follows:

$$\Gamma_{pK} = A_{pK}\gamma_{pK}\,\bar{X}\begin{pmatrix} lsj \\ lsj \\ pK1 \end{pmatrix} , \qquad (4')$$

where

$$\gamma_{01} = 1/\sqrt{7}, \quad \gamma_{10} = -1/2\sqrt{21}, \quad \gamma_{21} = 1/\sqrt{42},$$

$\bar{X}$ is a Wigner 9-j symbol, and the lsj are the quantum numbers of the conduction electrons [Eq. (3)]. The orbital operators $U_q^{[p]}$ are written as irreducible tensors that transform as the spherical harmonics. We define these operators by specifying that their reduced matrix elements are

$$\langle l_f \,||\, U^{[p]} \,||\, l_f \rangle = (-1)^{p/2}.$$

Their ranks p are limited only by the orbital angular momentum l_f of an electron in the open shell of the magnetic ion, e.g., for f electrons $l_f = 3$ and $p \le 6$. The operator $S^{[K]}$ is a constant for $K = 0$, and for $K = 1$ is the spin $\vec{S}$ in spherical-tensor notation. If the interaction consisted of only direct exchange and if the ion had only one magnetic electron, the parameters α and β would simply be unity.

The hyperfine interaction between a nuclear spin and the surrounding electrons (conduction or anion) is given as[16]

$$\mathcal{3C}_{\text{hf}} = 2\mu_B g_N \mu_N$$

$$\times \left(\frac{\vec{l}}{r^3} - \frac{\sqrt{10}}{r^3}\,[C^{[2]} \times s^{[1]}]^{[1]} + \frac{8\pi}{3}\,\delta(\vec{r})\vec{s} \right) \cdot \vec{I}, \qquad (5)$$

where μ_B is the Bohr magneton, μ_N is the nuclear magneton, and g_N is the gyromagnetic ratio for the nuclear spin. The three terms of Eq. (5) correspond to the orbital, spin-dipolar, and contact interactions, respectively. $C_m^{[2]}$ is a spherical harmonic,[17] and the product $[C^{[2]} \times s^{[1]}]_q^{[1]}$ transforms as a vector. The hyperfine interaction can be put into a form similar to Eq. (4):

$$\mathcal{3C}_{\text{hf}} = 2\mu_B g_N \mu_N \sum_{pK} [B^{[1]}(pK) \times I^{[1]}]^{[0]}, \qquad (5')$$

where

$$B^{[1]}(10) \equiv B_{10}\vec{l} = (\sqrt{3})\,\frac{\vec{l}}{r^3},$$

$$B^{[1]}(01) \equiv B_{01}\vec{s} = \frac{8\pi}{\sqrt{3}}\,\delta(\vec{r})\vec{s},$$

$$B^{[1]}(21) \equiv B_{21}[C^{[2]} \times s^{[1]}]^{[1]}$$

$$= -(\sqrt{30})\,\frac{1}{r^3}\,[C^{[2]} \times s^{[1]}]^{[1]},$$

and all other $B^{[r]}(pK)$ are zero.

The lowest-order coupling between the $4f$ electrons and the nuclear spin of a neighboring anion comes from the second-order perturbation of the ground-state energy of the system[11,12,18]:

$$E^{(2)} = \sum_{\vec{k}jm}^{\text{filled bands}} \sum_{\vec{k}'j'm'}^{\text{empty bands}} \frac{1}{E_{\vec{k}jm} - E_{\vec{k}'j'm'}} \left(e^{i(\vec{k}-\vec{k}')\cdot(\vec{R}_A - \vec{R}_B)} \langle \varphi\vec{k}jm | \mathcal{3C}_{sf} | \varphi'\vec{k}'j'm' \rangle \langle Im_I\vec{k}'j'm' | \mathcal{3C}_{\text{hf}} | Im_I'\vec{k}jm \rangle \right.$$

$$\left. + e^{i(\vec{k}-\vec{k}')\cdot(\vec{R}_B - \vec{R}_A)} \langle Im_I\vec{k}jm | \mathcal{3C}_{\text{hf}} | Im_I'\vec{k}'j'm' \rangle \langle \varphi\vec{k}'j'm' | \mathcal{3C}_{sf} | \varphi'\vec{k}jm \rangle \right). \qquad (6)$$

The vectors $\vec{R}_\alpha$ give the positions of the rare-earth ion and nuclear spin with respect to an arbitrary point in the crystal. We define an effective-coupling Hamiltonian $\mathcal{K}^{(2)}$ by

$$E^{(2)} \equiv \langle \varphi Im_I | \mathcal{K}^{(2)} | \varphi' Im_I' \rangle .$$

In the energy denominator of Eq. (6) we have neglected energy differences between the states φ and φ' of the $4f$ electrons. This is not a serious omission because we will be evaluating the coupling Hamiltonian only for crystal field states of the $4f$ electrons φ and φ' whose energy difference is small compared to the Fermi energy of the conduction electrons.

We have derived an explicit form for the coupling Hamiltonian by using wave functions like Eq. (3) for the conduction electrons, and the Hamiltonians (4) and (5) for the ion–conduction-electron (s-f) and hyperfine interactions. By using Racah's algebra[15] the interaction can be written as a scalar triple product:

$$\mathcal{K}^{(2)} = g_N \mu_N \sum_{pKr} \sum_\Lambda [\xi^{[\Lambda]}(pKr, \vec{R}_{AB}) \times J^{[r]}(pK) I^{[1]}]^{[0]} ,$$
(7)

where

$$J_m^{[r]} \equiv \frac{1}{\gamma_{pK}} [U^{[p]}(\vec{L}) \times S^{[K]}]_m^{[r]}$$

is a coupled product which refers to the orbital and spin operators for the $4f$ electrons. The parameters γ_{pK} are defined in Eq. (4'). The coefficients $\xi_m^{[\Lambda]}$ have been arranged to transform under rotations as the spherical harmonics and depend on the interionic distance $\vec{R}_{AB} \equiv \vec{R}_A - \vec{R}_B$. These coefficients contain sums over conduction-electron states [see Eq. (6)], the exchange integrals Γ_{pK}, the expectation values $\bar{B}_{p'K'}$ of the hyperfine-interaction operators $B_{p'K'}$ for electrons in the conduction-band states, and Wigner 3-j, 6-j, and 9-j symbols that are used to couple the orbital and spin operators into scalar triple products. The primary condition on the ranks of the operators is that their sum $p + K$ must be odd. In addition, if the operator $J^{[r]}(pK)$ is used only on states within one manifold of total angular momentum, the rank r also must be odd. For f electrons $0 \le p \le 6$, $K = 0, 1$, and $1 \le r \le 7$. Each coupling coefficient $\xi^{[\Lambda]}(pKr)$ contains a sum over the coefficients $\bar{B}_{p'K'}$, and can be written in the form

$$\xi^{[\Lambda]}(pKr, \vec{R}_{AB}) = \sum_{p'K'} b^{(\Lambda)}(pKr, p'K'1; \vec{R}_{AB}) .$$
(8)

In general, the dependence of the coupling $\xi^{[\Lambda]}(\hat{R}_{AB})$ on the orientation of the interionic pair axis $\hat{R}_{AB}$ is a complicated function. In addition to the anisotropy attendant to the A and B sites being at different spatial points, anisotropy is also present in the band electron wave functions. If

we make the spherical-band approximation and also neglect the dependence of the conduction-electron energies $E_{\vec{k}jm}$ on the spatial quantum number m, we can average over all angles in $\vec{k}$ space and sum over m and m' [see Eq. (6)]. In this approximation we find

$$\xi^{[\Lambda]}(pKr, \vec{R}_{AB}) = \xi^{[\Lambda]}(pKr, |R_{AB}|) C^{[\Lambda]}(\Omega_{AB}) .$$

If the spin-orbit coupling of the conduction electrons is weak, their energy is independent of the quantum number j as well as m, i.e., $E_{\vec{k}jm} = E_{\vec{k}}$. By summing over j and j' as well as m and m' (which is equivalent to summing over m_l and m_s), we find that the coupling coefficients $\xi^{[\Lambda]}$ are simplified through the relation

$$b^{(\Lambda)}(pKr, p'K'1) = b^{(\Lambda)}(pKr, p'K1)\delta(K, K')\delta(p, p', \Lambda) .$$
(8')

The function $\delta(p, p', \Lambda)$ vanishes unless $|p - p'| \le \Lambda \le p + p'$.

The coupling Eq. (7) contains isotropic ($\Lambda = 0$) *and* anisotropic ($\Lambda \ne 0$) terms. In analyzing the data on the rare-earth compounds, we will make the simplifying assumption of considering only isotropic coupling, i.e., take only the terms $\Lambda = 0$ and $r = 1$:

$$\mathcal{K}^{(2)} = g_N \mu_N \sum_{pK} \xi^{[0]}(pK1, \vec{R}_{AB})[J^{[1]}(pK) \times I^{[1]}]^{[0]} .$$
(7')

If we restrict the use of this Hamiltonian to states within one manifold of the total angular momentum J of the $4f$ electrons, the coupling takes on the simple form

$$\mathcal{K}^{(2)} = \frac{g_N \mu_N}{\sqrt{3}} [(g_J - 1)\xi^{[0]}(011, \vec{R}_{AB})$$
$$+ (2 - g_J)\xi^{[0]}(101, \vec{R}_{AB})$$
$$+ c_n \xi^{[0]}(211, \vec{R}_{AB})] \vec{J} \cdot \vec{I} ,$$
(9)

where

$$c_n \equiv \frac{1}{\gamma_{21}} \frac{\langle J || [U^{[2]}(L) \times S^{[1]}]^{[1]} || J \rangle}{\langle J || J^{[1]} || J \rangle} .$$

We have included the subscript n as a reminder that this coefficient depends on the number n of $4f$ electrons. Values for c_n together with $(g_J - 1)$ and $(2 - g_J)$ are given in Table I for all ions in the rare-earth series. For conduction electrons in spin-orbit coupled states, Eq. (8) gives

$$\xi^{[0]}(pK1) = b^{[0]}(pK1, 011) + b^{[0]}(pK1, 101)$$
$$+ b^{[0]}(pK1, 211) ,$$
(10)

whereas for conduction electrons in states with negligible spin-orbit coupling

$$\xi^{[0]}(pK1) = b^{[0]}(pK1, pK1) .$$
(10')

Thus, without spin-orbit coupling, the interaction term $\xi^{[0]}(pK1)$ depends only on the term $\bar{B}_{pK}$ [the

TABLE I. Constants for trivalent rare-earth ions.

	Ce	Pr	Nd	Pm	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb
J	5/2	4	9/2	4	5/2	7/2	6	15/2	8	15/2	6	7/2
$(g_J - 1)J$	$-5/14$	$-4/5$	$-27/22$	$-8/5$	$-25/14$	7/2	3	5/2	2	3/2	1	1/2
$(2 - g_J)J$	20/7	24/5	126/22	28/5	30/7	0	3	5	6	6	5	3
$c_n J$	$-6/7$	$-52/75$	$-63/242$	14/55	13/21	0	$-1/2$	$-1/2$	$-1/5$	1/5	1/2	1/2

expectation value of the operator B_{pK} defined in Eq. (5′)], while with spin-orbit coupling, each term $\xi^{[0]}(pK1)$ depends on all three terms $\bar{B}_{01}$, $\bar{B}_{10}$, and $\bar{B}_{21}$. In either case, the form of the effective interaction Eq. (9) is the *same*. It is only in the interpretation of the coefficients $\xi^{[0]}$ that the spin-orbit coupling of the conduction-electron states makes a difference.

We have considered other processes which produce a hyperfine field. Instead of polarizing conduction electrons, the $4f$ electrons can polarize the anion electrons through a direct or superexchange interaction. In this case it is the polarized anion electrons which create a transferred hyperfine field. Another possibility is a three-step process: The s-f exchange interaction polarizes the conduction electrons, which in turn interact with the anion electrons. The polarized anion electrons then produce the major contribution to the transferred hyperfine field. Supertransferred hyperfine-interaction processes have also been considered. Whereas all these processes enter in varying orders of perturbation on the ground state of the system, they all have the same form of coupling between the magnetic ion and the nuclear spin as in Eq. (7). However, the interpretation of the coefficients $\xi^{[\Lambda]}(pK\gamma)$ does depend on the details of the process considered. For example, if the electrons which create the hyperfine field have orbital character, then the coupling coefficient $\xi^{[0]}(pK1)$ contains contributions from $\bar{B}_{01}$, $\bar{B}_{10}$, and $\bar{B}_{21}$ while for orbital singlet states only the Fermi contact-interaction term $\bar{B}_{01}$ contributes.

Whether all coefficients $b^{[0]}(pK1, p'K'1)$ exist or only $b^{[0]}(pK1, pK1)$ exists depends on the details of the intermediate coupling, i.e., whether it is direct exchange ($p = p'$, $K = K'$) or indirect exchange that is involved and whether the intermediate electrons are in spin-orbit coupled states. When the electrons which create the hyperfine field at the anion have no orbital character but there is spin-orbit coupling of the conduction electrons about the rare-earth sites, the hyperfine coupling $\mathcal{K}^{(2)}$ *will* depend on the expectation values $\langle \vec{L} \rangle_{RE}$ and $\langle [U^{[2]}(L) \times S^{[1]}]^{[1]} \rangle_{RE}$ of the rare-earth ion. If, in addition to no orbital character at the anion site, there is no spin-orbit coupling of the intermediate electrons, the isotropic coupling, Eq. (7), does not have any orbital contributions for the simple

process considered above. However, there is an orbital contribution to the anisotropic ($\Lambda \neq 0$) bilinear coupling. For more complicated indirect processes the hyperfine coupling in the above case will have orbital contributions to the isotropic hyperfine coupling, but only the term $\langle [U^{[2]}(L) \times S^{[1]}]^{[1]} \rangle_{RE}$ makes a dominant contribution when the intermediate states are not spin-orbit coupled.

III. HYPERFINE FIELD

The hyperfine field H_{hf} acting on a nuclear spin I due to the *time-averaged* magnetic moments of the surrounding ions is defined through the hyperfine Hamiltonian

$$\mathcal{K} = g_N \mu_N \vec{H}_{hf} \cdot \vec{I} \ .$$

By comparing this expression to Eq. (9), we find the hyperfine field at the anion site is given as

$$\vec{H}_{hf} = [(g_J - 1)H_{01} + (2 - g_J)H_{10} + c_n H_{21}]\langle \vec{J} \rangle \ , \quad (11)$$

where

$$H_{pK} = \frac{1}{\sqrt{3}} \sum_{\vec{R}_{AB}} \xi^{[0]}(pK1, \vec{R}_{AB})$$

and $\langle J \rangle$ is the thermal expectation value of the total angular momentum of the rare-earth ion. The lattice sum in Eq. (11) is over all magnetic sites with the nuclear spin at the origin. We see that there are contributions to the hyperfine field from the orbital angular momentum of the rare-earth $4f$ electrons. For intermediate states $\Psi_{\vec{k}\lambda}$, $\Psi_{\vec{k}'\lambda'}$ with little orbital character, e.g., plane-wave states, the orbital contributions H_{10} and H_{21} are small compared to the spin term H_{01}.[11,19] However, when the intermediate states have appreciable orbital character these terms may be important. This will be especially true when the intermediate electrons are in spin-orbit coupled states. If we assume the H_{pK} are constant for a given series of rare-earth compounds, the transferred hyperfine field [Eq. (11)] has two additional parameters available when compared to Eq. (2). It will naturally be possible to improve the fit to the data. However, the three-parameter expression is required to fit many data points which vary substantially in magnitude and, in some cases, cover both the heavy and the light rare earths. Therefore these fits provide a fair test of the existence of the additional terms H_{10} and H_{21} in the hyperfine field, Eq. (11).

If the exchange interaction, Eq. (4), is much stronger than the crystal field interaction, we may take $\langle J_z \rangle = J$. However, in a majority of the systems we studied this approximation is inadequate. Instead, $\langle J_z \rangle$ is a thermal average of J_z over the energy levels of the rare-earth ion:

$$\langle J_z \rangle = \frac{\sum_j e^{-E_j/kT} \langle j | J_z | j \rangle}{\sum_j e^{-E_j/kT}} \quad ,$$

where E_j is the crystal field plus exchange energy. This thermal average is related to the experimental magnetic moments of the rare-earth ions as follows:

$$\mu_{expt} / \mu_{FI} = \langle J_z \rangle / J \quad ,$$

where μ_{expt} is the experimental magnetic moment of the rare earth and μ_{FI} is the free-ion value. Equation (11) is then written as

$$H_{hf} = [(g_J - 1) H_{01} J + (2 - g_J) H_{10} J + c_n H_{21} J] \mu_{expt} / \mu_{FI} \; .$$
$$(12)$$

In deriving Eq. (12) we neglected the higher-degree contributions $r > 1$ [see Eq. (7)]. If these terms are important we would not find a simple linear relationship between the hyperfine field and the magnetization. Data on the variation of the hyperfine field with temperature would be useful to substantiate this point. However, at present few experimental data exist and it is not possible to verify the simple, linear dependence of H_{hf} on μ_{expt}. (One should note that Sm and Eu are exceptions. Even when we consider only a linear, isotropic hyperfine interaction, the hyperfine field is not directly proportional to the magnetization. In the Appendix we discuss the case of Eu.)

IV. RESULTS

We have used Eq. (12) to fit the hyperfine-field data on several series of rare-earth compounds. In Table II the hyperfine fields obtained from a least-squares fit to the data[20] by using Eq. (12) are compared with experimental results on the rare-earth compounds, RAs, RP, RAl$_2$, RIr$_2$, R_2Sn, Hf as a dilute impurity in the rare-earth metals, and Sn in rare-earth iron garnets. Equation (12) has been used for those cases where the values μ_{expt} are known.[21] When such data are not available, we have assumed $\mu_{expt} = \mu_{FI}$. In all cases, the variation of H_{hf} with the rare-earth ion is rather well reproduced. The calculated and experimental points are compared with data for the compounds RP in Fig. 1 and for the impurity case RHf in Fig. 2. In the latter case, error bars are quite large. However, the rapid decrease of the hyperfine field, becoming zero long before Lu is reached, is quite clear and can easily be understood as arising from a simple cancellation of terms in Eq. (11).

The supertransferred hyperfine field of ^{119}Sn in a series of rare-earth iron garnets has been measured recently and analyzed to provide the contribution arising directly from the rare-earth ions.[22] Anisotropic exchange is important in these systems,[23,24] but no definitive parameters have been determined for the anisotropy in the exchange interaction. We have fit the data to Eq. (12) to
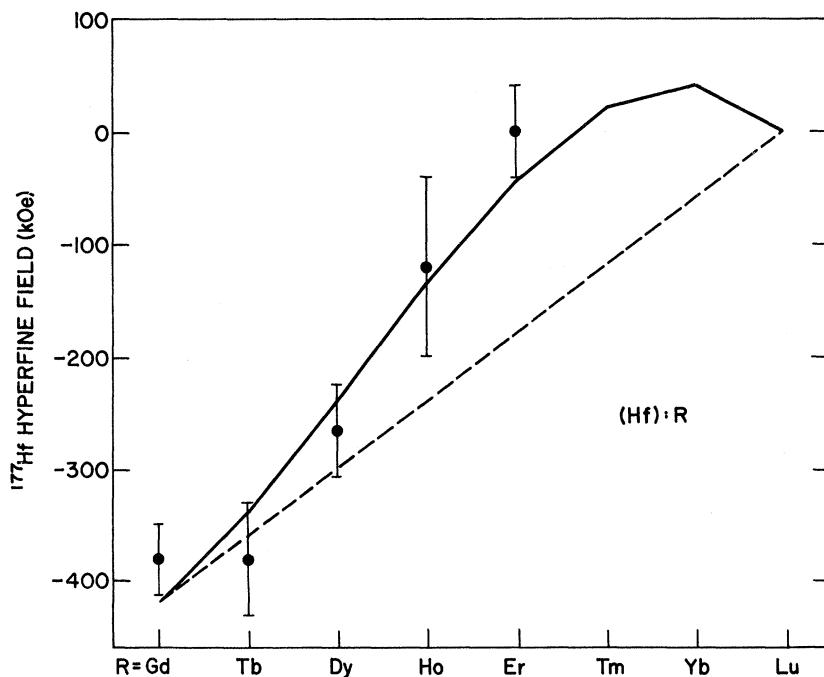

FIG. 2. Comparison of experimental and calculated hyperfine fields for Hf as an impurity in the heavy rare-earth metals. Experimental points (solid circles) are obtained by perturbed angular-correlation measurements on ^{177}Hf (Ref. 3). Calculated curves are for Eq. (2) (dashed line) with $H_s = -120$ kOe and Eq. (12) (solid line) with $\mu_{expt} = \mu_{FI}$ and parameters given in Table III.

TABLE II. Comparison of calculated (calc) hyperfine fields using parameters given in Table III and experimental (expt) hyperfine fields. Errors are given for experimental results only if available from the indicated reference. All fields are in units of kOe.

R =		Ce	Pr	Nd	Sm[a]	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
RP	expt[b]	20	28	36	32	−73	−67	−48	−35	−24	−18	−10	−7
	calc[c]	18	28	35	39	−67[d]	−67	−49	−35	−25	−17	−11	−7
RAl$_2$	expt[b]	10	16	20			−45	−36	−26	−32	−19	−12	
	calc	11	16[c]	16	25[c]		−49	−35	−28	−19	−17	−10	−7[e]
RAs	expt[b]	37	55	71	70		−119					−22	
	calc[c]	37	57	69	68		−119	−82	−57	−41	−30	−22	−13
R$_2$Sn	expt[e]						−289 ± 10	−184 ± 8	−142 ± 12	−67 ± 25	−55 ± 25		
	calc[c]	85	136	166	169		−287	−200	−139	−98	−69	−48	−27
RIr$_2$	expt[f]		46 ± 9	48 ± 9	89 ± 13		−192 ± 14	−167 ± 10	−93 ± 10	−40 ± 8	−34 ± 5		
	expt[g]				93 ± 6		−238 ± 13	−164 ± 8	−126 ± 6	−64 ± 5			
	calc	11[c]	34	52	58		−219	−146	−107	−66	−27	−2	3
R(Hf)	expt[h]						−380 ± 30	−380 ± 50	−265 ± 40	−120 ± 80	0 ± 40		
	calc	31	136	240	324		−420	−340	−240	−136	−44	20	40
RIG(Sn)	expt					−5	−28	−14	−4	−1.5	−4[i]	−0.5	−0.5
	calc					−6[j]	−29	−13	−5	−1.5	−1	−0.5	−0.5

[a] The values for Sm are calculated by considering only the $J = \frac{5}{2}$ ground state.
[b] Reference 2.
[c] Insufficient data to correct for crystal fields.
[d] Eu^{2+} is assumed to give a value identical with Gd^{3+}.
[e] Reference 6.
[f] Reference 5.
[g] Reference 4.
[h] Reference 3.
[i] See caption to Fig. 3.
[j] See Appendix.

demonstrate that even isotropic orbital contributions to the supertransferred hyperfine field can explain the discrepancies between the observed fields and those calculated by considering only spin polarization, Eq. (2). In Table II and in Fig. 3, we give the results of fitting Eq. (12) to the data.[22,25] While the isotropic terms can describe the data quite well, the parameters H_{pK} will not be meaningful if future determinations of the anisotropic exchange show that it is as large as the isotropic exchange.

Values for the parameters H_{01}, H_{10}, and H_{21} obtained for the various systems are listed in Table III. Because of the different crystal structures, it is not possible to make a detailed comparison of the results. However, some general comments can be made:

(i) The contributions to the hyperfine field H_{10} and H_{21} are of importance when the conduction electrons (or those electrons which produce the hyperfine field) have significant orbital character. This dependence on the orbital character can be seen by comparing the values for the parameters H_{10} and H_{21} with H_{01} given in Table III. For $R\text{Al}_2$, the aluminum ion has p-type valence electrons and H_{21} is approximately 30% of H_{01}; for $R\text{Ir}_2$ (d outer electrons) H_{21} is over 60% of H_{01}. In general the hyperfine-field coefficient H_{21} is comparable with the spin coefficient H_{01}, about 50%, while the orbital coefficient H_{10} is smaller, i.e., about 10%. One should not be misled, however, into thinking this infers that the orbital term may be neglected. In fact, the hyperfine contributions $(2 - g_J)H_{10}J$ and $c_n H_{21}J$ are frequently comparable in magnitude, as is illustrated in Table IV by the $R\text{P}$ system.

(ii) Levy has used Eq. (4) to describe the spin-

disorder resistivity in the $R\text{Al}_2$ compounds,[13] and the depression of the superconducting transition temperature of LaAl_2 when other rare-earth atoms are added.[14] The values for the exchange constants Γ_{pK} thus obtained are also given in Table III. One sees that the relative signs and relative magnitudes of these parameters are in general agreement with the corresponding constants H_{pK} obtained from the present work. In particular, the ratios of the exchange parameters for $R\text{Al}_2$ derived from the decrease of the superconducting transition temperature $\Gamma_{21}/\Gamma_{01} = 0.38$ and $\Gamma_{10}/\Gamma_{01} = -0.05$ are in good agreement with the ratios of the hyperfine-field coefficients $H_{21}/H_{01} = 0.29$ and $H_{10}/H_{01} = -0.04$.

There is no *a priori* reason for these ratios to agree. In general we find for spin-orbit coupled intermediate states

$$\frac{H_{pK}}{H_{01}} = \frac{\sum_{p'K'} \bar{b}^{[0]}(pK1, p'K'1)}{\sum_{p'K'} \bar{b}^{[0]}(011, p'K'1)} \ , \tag{13}$$

where

$$\bar{b}^{[0]} \equiv \sum_{\vec{R}_{AB}} b^{[0]}(pK1, p'K'1; \vec{R}_{AB}) \ ,$$

whereas for no spin-orbit coupling we find

$$\frac{H_{pK}}{H_{01}} = \frac{\bar{b}^{[0]}(pK1, pK1)}{\bar{b}^{[0]}(011, 011)} \ . \tag{13'}$$

When we make the assumption of retaining only the s partial wave in the expansion of the plane wave $e^{i\vec{k}\cdot\vec{r}}$, the coupling coefficients in Eq. (10) can be factored:

$$b^{[0]}(pK1, p'K'1; \vec{R}_{AB}) = \Gamma_{pK}\tilde{B}_{p'K'}f(R_{AB}) \ ,$$

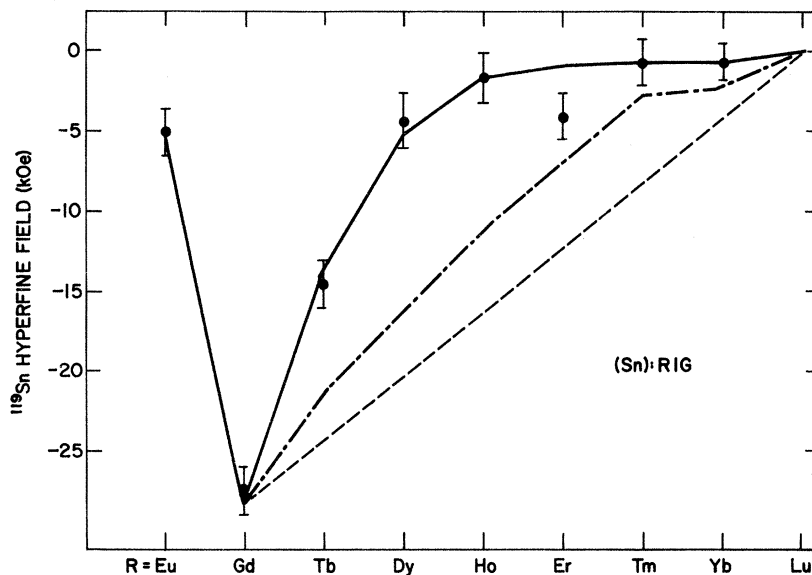where Γ_{pK} is an s-f exchange integral [Eq. (4')] and

FIG. 3. Comparison of experimental and calculated supertransferred hyperfine fields acting on Sn nuclei in rare-earth iron garnets. Experimental points (solid circles) are obtained by Mössbauer-effect measurements on ^{119}Sn (Ref. 22). The experimental point for ErIG is suspect since the data were analyzed on the assumption of [111] as the easy direction of magnetization, whereas [001] is now known to be the proper direction (see Ref. 25). The calculated curves are for Eq. (2) (dashed line) with $H_s = -8.3\,\text{kOe}$, Eq. (2) with crystal field corrections (dash-dot line) taking μ_{expt} from Ref. 28, and Eq. (12) (solid line) using parameters given in Table III. The point for EuIG is calculated using Eq. (A2).

TABLE III. Hyperfine-field constants H_{pK} and exchange coupling constants for various rare-earth intermetallic systems. Values for H are in kOe, values for Γ are in 10^{-2} eV.

Compound	H_{01}	H_{10}	H_{21}	H_{10}/H_{01}	H_{21}/H_{01}	Γ_{01}	Γ_{10}	Γ_{21}	Γ_{10}/Γ_{01}	Γ_{21}/Γ_{01}
RAl$_2$	-14	0.5	-4	-0.04	0.29	7.3 [a]	-0.34 [a]	2.8 [a]	-0.05	0.38
						7.1 [b]	-0.71 [b]	0.91 [b]	-0.10	0.13
RIr$_2$	-64	8	40	-0.12	-0.64					
RP [c]	-19	2	-6	-0.10	0.31					
RAs [c]	-34	4	-16	-0.12	0.48					
R_2Sn [c]	-82	10	-32	-0.12	0.39					
R(Hf)	-120	20	80	-0.17	-0.67					
RIG(Sn)	-8.3	2.1	-6.9	-0.26	0.83					

[a]Reference 14.　　　　[b]Reference 13.　　　　[c]Insufficient data available to correct for crystal fields.

$$\tilde{B}_{p'K'} = \overline{B}_{p'K'} \overline{X} \begin{pmatrix} l & s & j \\ l & s & j \\ p' & K' & 1 \end{pmatrix} .$$

The function $f(R_{AB})$ represents an integral over two spherical Bessel functions of order zero. By using these factorized coefficients, we find that the ratios for the hyperfine field are simplified. For intermediate states with spin-orbit coupling

$$\frac{H_{pK}}{H_{01}} = \frac{\Gamma_{pK}}{\Gamma_{01}} ,$$

while for no spin-orbit coupling we find

$$\frac{H_{pK}}{H_{01}} = \frac{\Gamma_{pK}}{\Gamma_{01}} \times \frac{\tilde{B}_{pK}}{\tilde{B}_{01}} .$$

There is no general reason for the ratios $\tilde{B}_{pK}/\tilde{B}_{01}$ to be close to unity. In fact, one generally expects $\tilde{B}_{01}$, which arises from the contact interaction, to be much larger than the other terms. Therefore, the aforementioned approximate agreement between the ratios of the hyperfine fields and the exchange parameters supports the previous observation[14] that the bands in RAl$_2$ are spin-orbit coupled. In this way we see that hyperfine-field data provide information on the exchange interactions which is compatible with that obtained from very different phenomena.

In conclusion it should be noted that diverse phenomena have been analyzed with Eq. (4): Curie points, resistivity, depression of superconducting transition points, and hyperfine fields. The ability

of the theory to explain results which not only are rather different but also depend in different ways on the pertinent parameters is a strong confirmation of its importance.

APPENDIX: HYPERFINE FIELD ACTING ON Sn^{119} IN EUROPIUM IRON GARNET

In the rare-earth series samarium and europium are special cases. Their J levels are close enough so that one should consider the admixture of other levels due to various perturbations. Here we consider europium.

The nominal ground state of Eu^{3+} is $^7F_0$. It is nonmagnetic and without a perturbation coupling in the excited J states, the ground state would not produce a hyperfine field. In europium iron garnet the europium-iron exchange interaction is sufficiently strong to admix excited states into the $^7F_0$ ground state.[26] By using Eq. (7') and the definition of the hyperfine field H_{pK}, Eq. (11), we write the hyperfine field on tin nuclei in EuIG as

$$\vec{H}_{hf} = \langle \vec{S} \rangle H_{01} + \langle \vec{L} \rangle H_{10}$$

$$+ \frac{1}{\gamma_{21}} \langle [U^{[2]} \times S^{[1]}]^{[1]} \rangle H_{21} . \quad (A1)$$

The angular brackets denote the expectation values of the operators in the ground state of europium. If one considers anisotropic terms in the hyperfine field $[\Lambda \neq 0,$ Eq. (7)], an additional contribution to Eq. (A1) enters, $\langle [U^{[1]} \times S^{[1]}]^{[1]} \rangle$. However, for the isotropic hyperfine field, this term does not enter because the corresponding hyperfine interac-

TABLE IV. Contributions to the ^{31}P hyperfine field in RP compounds, calculated from the parameters of Table III.

	CeP	PrP	NdP	SmP	GdP	TbP	DyP	HoP	ErP	TmP	YbP
$(g_J-1)H_{01}J$	7	15	23	34	-67	-58	-48	-38	-28	-18	-10
$(2-g_J)H_{10}J$	6	9	11	9	0	6	10	12	12	10	6
$c_n H_{21}J$	5	4	1	-4	0	3	3	1	-1	-3	-3
Total H_{hf}	18	28	35	39	-67	-49	-35	-25	-17	-11	-7

tion, $B^{[1]}$ (11) [see Eq. (5′)], does not exist.

We must have enough knowledge of the ground state to evaluate the averages in Eq. (A1). From the analysis of Wolf and Van Vleck[26] we find that the magnetization for temperatures of 77 °K and below can be accounted for by contributions from the off-diagonal matrix elements between the levels $J = 0$ and $J = 1$. In this approximation we find that[26,27]

$$M_{\mathrm{Eu}} = \mu_B \langle L_z + 2 S_z \rangle = \mu_B \langle S_z \rangle = - \mu_B \langle L_z \rangle$$

$$= 16 \mu_B^2 H_{\mathrm{exch}} / \Delta ,$$

where Δ is the energy of the first excited $^7F_1$ Eu^{3+} ionic state. With $\Delta = 480$ °K and $\mu_B H_{\mathrm{exch}}/k = 22$ °K, the calculated and experimental moments agree very well.[28,29] The hyperfine field acting on Eu^{3+} nuclei in EuIG is given by[30]

$$H_{\mathrm{eff}} = 2 \mu_B \left\langle \frac{1}{r^3} \right\rangle \langle N_z \rangle = - \frac{80 \mu_B^2 H_{\mathrm{exch}}}{3\Delta} \left\langle \frac{1}{r^3} \right\rangle .$$

Since $\vec{N} = \vec{L} - (\sqrt{10}) [C^{[2]} \times S^{[1]}]^{[1]}$, one finds that

$$\frac{1}{\gamma_{21}} \langle [C^{[2]} \times S^{[1]}]^{[1]} \rangle = - (\sqrt{\tfrac{7}{60}}) \langle S_z \rangle$$

and

$$\frac{1}{\gamma_{21}} \langle [U^{[2]} \times S^{[1]}]^{[1]} \rangle = - \tfrac{1}{4} \langle S_z \rangle .$$

This last result has been confirmed also by a straightforward calculation. Within the above approximations one obtains for the hyperfine field of the Sn^{119} nuclei in EuIG:

$$H_{\mathrm{hf}}(\mathrm{Eu}) = (H_{01} - H_{10} - \tfrac{1}{4} H_{21}) \langle S_z \rangle . \qquad (A2)$$

Using the values of the parameters H_{pK} given in Table III together with[29] $M_{\mathrm{Eu}} = 0.74 \mu_B$, we find

$$H_{\mathrm{hf}}(\mathrm{Eu}) = - 6.5 \text{ kOe.}$$

This is in very good agreement with the experimental value of -5 kOe.

A final note of caution. The value found by using Eq. (A2) is very close to that one finds had one neglected the orbital contributions H_{10} and H_{21}. This is due to a near cancellation of these contributions for europium. It would be incorrect to neglect these terms *a priori*.

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