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Orbital and spin polarizations of conduction electrons in rare-earth intermetallic compounds. Theory

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Recent experiments on rare-earth intermetallic compounds have given us data on the contribution from conduction electrons to the magnetization and hyperfine fields at rare-earth nuclei. Analyses based on isotropic bilinear exchange interactions between the $4f$ and conduction electrons have not been able to explain the systematic variation of these contributions across the rare-earth series. To explain these variations it is necessary to take into account the full $4f$ conduction-electron exchange interaction (higher-rank couplings) and the crystallographic symmetry at the rare-earth sites. In some cases, it is necessary to include the spin-orbit coupling of the conduction electrons. The conduction electrons in the rare-earth intermetallic compounds of interest are primarily of $5d$ and $6s$ character. In this paper we derive expressions for the orbital and spin polarizations of these conduction electrons and their contribution to the hyperfine field and magnetization. We take full account of the site symmetry, which is cubic for the compounds of interest, and the complete $4f$-$5d$ conduction-electron interaction.

I. INTRODUCTION

Two recent series of experiments on rare-earth dialuminides have provided us with evidence that there is an orbital as well as spin polarization of the conduction electrons in these intermetallic compounds. We expect this phenomenon to be relatively widespread in many rare-earth intermetallic compounds, e.g., the RAg, RZn series. In this article we give a complete theoretical analysis of these orbital effects first from a group-symmetry viewpoint and then on the basis of specific models for the conduction electrons and the rare-earth conduction-electron interaction. In an ulterior paper the expressions developed in this article are planned to be used to analyze the extant data and determine the size of the orbital effects coming from the conduction electrons.

From polarized neutron-diffraction studies on the rare-earth dialuminides ($R\mathrm{Al}_2$) at temperatures below their Curie points, Boucherle and Schweizer determined the magnetic form factors for several of the rare earths (R: Nd, Sm, Ho).[1] By analyzing their data they have decomposed the form factor into one part coming from the highly localized $4f$ electrons and another more diffuse part coming from the $5d$ and $6s$ conduction electrons. By extrapolating the form factor down to zero scattering vector and comparing their results with magnetization measurements, they have decomposed the total magnetization into a part due to the $4f$ electrons M_{4f} and another part from the conduction electrons M_{cond}. In addition by fitting the magnetic form factors to their data, Boucherle and Schweizer have been able to determine the wave functions for the $4f$ electrons in the magnetically ordered states of the compounds.

We have analyzed the contributions of the conduction electrons and find that (i) there are orbital as well as spin polarization contributions to the magnetization from these electrons and (ii) these contributions are not simply proportional to the orbital and spin moments of the rare-earth $4f$ electrons.[2]

From a different viewpoint, Berthier *et al.*,[3] Vijayaraghavan *et al.*,[4] and Dintelmann *et al.*[5] used nuclear magnetic resonance to measure the hyperfine fields at the rare-earth sites in the dialuminides (R: Pr, Nd, Sm, Gd, Dy, Tb, and Er). Berthier, Devine, and Belorizky[3] used a decomposition of the hyperfine field at the rare-earth nucleus in one part coming directly from the $4f$ electrons H_{4f}, another part from the conduction electrons at the rare-earth sites, i.e., the self-polarization field H_{sp}, and a third part from the moments at different sites, i.e., the transferred hyperfine field. From their preliminary analysis of the data they concluded that the variation of the self-polarization field across the rare-earth series could not be explained by only a spin polarization of the conduction electrons; it is necessary to admit an orbital polarization of the electrons. In addition they found that H_{sp} is not directly proportional to the orbital and spin moments of the $4f$ electrons. However their analysis was hampered by their inability to reliably separate the $4f$ and conduction-electron contributions to the hyperfine field, because the $4f$ contribution to the magnetic moment or $\langle J_z \rangle_{4f}$ is only known for the four rare earths cited in the work of Boucherle and Schweizer, i.e., R: Nd, Sm, Gd, and Ho. Therefore before we can separate out the self-polarization field it is necessary to have a reliable extrapolation scheme to determine the $\langle J_z \rangle_{4f}$'s for the remaining rare earths. Although the total magnetic moment per rare earth is known from magnetization measurements, the contribution from conduction electrons M_{cond} must be removed to determine $\langle J_z \rangle_{4f}$. The results of Berthier *et al.*[3] pointed to the need for a formula that gives us the variation across the rare-earth series of the conduction-electron contribution to the magnetization. In this way the analysis of the composition of the hyperfine field in these compounds is closely related to the studies of Boucherle and Schweizer which separate M_{4f} and M_{cond}.

Our principle aim in this article is to present various formulas which give the variations across the rare-earth series of the conduction-electron contributions to the magnetization, and hyperfine field at the rare-earth nucleus. As we have seen it is necessary to know the former in order to determine the latter. In Sec. II we use group-theoretical arguments with a minimum number of assumptions to obtain these variations as a function of the multipole moments of the $4f$ electrons. As many unknown parameters enter the expressions (compared to the data available) it is necessary to make further assumptions so as to reduce the number of unknown parameters. We show that by making additional assumptions about the general nature of the conduction electrons we are able to reduce the number of parameters. However, the general symmetry arguments presented in Sec. II do not provide a microscopic description of the mechanisms which give rise to the polarization and consequent contributions from conduction electrons to the magnetization and hyperfine fields. Therefore in Sec. III we present a calculation of these effects based on specific models of the conduction electrons and of the rare-earth conduction-electron interaction. Based on these models we are able to describe the variation of both M_{cond} and H_{sp} across the rare-earth series with seven parameters. A test of the validity of these formulas must wait till we have enough data on the $4f$ electron wave functions. Then we will be able to determine the ability of our formulas to accurately fit the experimental data on the variations across the rare-earth series of M_{cond} and H_{sp}.

The theory we develop in the following sections is valid for all rare-earth intermetallic compounds, but the expressions have been explicitly evaluated only for those compounds where the rare earth is in a site of cubic symmetry (O_h or T_d), e.g., RZn and RAl$_2$. The extension to other point-group symmetries is straightforward.

II. GROUP-THEORETICAL SYMMETRY ARGUMENTS

In this section we study the general form of the self-polarization hyperfine field H_{sp}, i.e., the additional hyperfine field from the $4f$ electrons at the same site as the nucleus in question due to the presence of conduction electrons. As part of this study we will also find the various terms that contribute to the orbital and spin polarizations of the conduction electrons.

To maintain maximum generality we make only the following assumptions:

(i) The self-polarization hyperfine field coming from the conduction electrons is induced by their exchange interaction with the $4f$ electrons. The generic form of the rare-earth conduction-electron (k-f) interaction is given as[6]

$$H_{k\text{-}f} = -\sum_{\mu} a_\mu \sum_{\nu=-\mu}^{\mu} (-)^\nu Y_{\mu-\nu}(\vec{L})\, Y_{\mu\nu}(\vec{l}) \times (2b_\mu \vec{S}\cdot\vec{s} + \tfrac{1}{2} c_\mu) \quad , \qquad (1)$$

where $\vec{L}$, $\vec{S}$ refer to the $4f$ shell and $\vec{l}$, $\vec{s}$ to the conduction electrons. The exchange interaction parameters a_μ can in principle be determined from the atomic Slater integrals G_k. The useful coupling coefficients b_μ and c_μ defined by Huang-Liu, Ling, and Orbach[6] are given in Table I for all rare earths. Note that we use the same convention as in Ref. 6, i.e.,

$$\mathrm{Tr}\, Y^*_{\mu\nu}(\vec{l})\, Y_{\mu\nu}(\vec{l}) = 1 \quad . \qquad (2)$$

With this normalization we have, for example,

$$Y_{10}(\vec{l}) = [l(l+1)(2l+1)/3]^{-1/2} l_z \quad . \qquad (2a)$$

The exchange Hamiltonian Eq. (1) is quite general as long as one limits ourself to the exchange of a pair of electrons at one site.

(ii) We assume that the conduction electrons near the Fermi surface do not have an orbital angular momentum exceeding $l = 2$. For rare-earth intermetallic compounds this assumption has been found to be valid. Band calculations have not shown that there are many elections of f or g character, but rather that conduction electrons have predominantly $6s$ and $5d$ character.

(iii) We consider cubic site symmetry, although the analysis could be readily adapted to other site symmetries.

While the explicit form of the hyperfine interactions will not be necessary in the following analysis it will be useful to help us determine the physical mechanisms giving rise to the various contributions to the self-polarization field. The Hamiltonian

TABLE I. Projection factors defined in Eq. (1).

$$\sum_i Y_{\mu\nu}(\vec{l}_i) = c_\mu Y_{\mu\nu}(\vec{L})$$

		L,S,J	c_0	c_1	c_2	c_3	c_4
Ce^{3+}	$4f^1$	$3\ \frac{1}{2}\ \frac{5}{2}$	1	1	1	1	1
Pr^{3+}	$4f^2$	5 1 4	2.5071	1.9821	1.0653	0	−0.9085
Nd^{3+}	$4f^3$	$6\ \frac{3}{2}\ \frac{9}{2}$	4.0883	2.5495	0.4438	−0.8876	−0.6371
Pm^{3+}	$4f^4$	6 2 4	5.4511	2.5495	−0.4438	−0.8876	+0.6371
Sm^{3+}	$4f^5$	$5\ \frac{5}{2}\ \frac{5}{2}$	6.2678	1.9821	−1.0653	0	0.9085
Eu^{3+}	$4f^6$	3 3 0	6	1	−1	1	−1
Gd^{3+}	$4f^7$	$0\ \frac{7}{2}\ \frac{7}{2}$	2.6458				
Tb^{3+}	$4f^8$	3 3 6	8	1	1	1	1
Dy^{3+}	$4f^9$	$5\ \frac{5}{2}\ \frac{15}{2}$	11.2821	1.9821	1.0653	0	−0.9085
Ho^{3+}	$4f^{10}$	6 2 8	13.6277	2.5495	0.4438	−0.8876	−0.6371
Er^{3+}	$4f^{11}$	$6\ \frac{3}{2}\ \frac{15}{2}$	14.9905	2.5495	−0.4438	−0.8876	0.6371
Tm^{3+}	$4f^{12}$	5 1 6	15.0428	1.9821	−1.0653	0	0.9085
Yb^{3+}	$4f^{13}$	$3\ \frac{1}{2}\ \frac{7}{2}$	13	1	−1	1	−1

$$\sum_i Y_{\mu\nu}(\vec{l}_i)\vec{s}_i = b_\mu Y_{\mu\nu}(\vec{L})\vec{S}$$

	b_0	b_1	b_2	b_3	b_4
Ce^{3+}	1	1	1	1	1
Pr^{3+}	1.2536	0.9910	0.5326	0	−0.4542
Nd^{3+}	1.3628	0.8498	0.1479	−0.2959	−0.2124
Pm^{3+}	1.3628	0.6374	−0.1109	−0.2219	0.1593
Sm^{3+}	1.2536	0.3964	−0.2131	0	0.1817
Eu^{3+}	1	0.1667	−0.1667	0.1667	−0.1667
Gd^{3+}	0.3780				
Tb^{3+}	1	−0.1667	−0.1667	−0.1667	−0.1667
Dy^{3+}	1.2536	−0.3964	−0.2131	0	0.1817
Ho^{3+}	1.3628	−0.6374	−0.1109	0.2219	0.1593
Er^{3+}	1.3628	−0.8498	0.1479	0.2959	−0.2124
Tm^{3+}	1.2536	−0.9910	0.5326	0	−0.4542
Yb^{3+}	1	−1	1	−1	1

describing the hyperfine interaction between the conduction electrons and the nuclear spin is

$$\mathcal{H}_{\mathrm{hf}} = A\,\{\vec{l} + \sqrt{20/7}[Y_2(\vec{l}) \times \vec{s}]^1 + k\,\vec{s}\} \cdot \vec{I}\ . \quad (3)$$

The first two terms describe the orbital and magnetic dipole interactions, while the last term represents the contact and core-polarization contributions. The product $[Y_2(\vec{l}) \times \vec{s}]^1$ represents a second-rank orbital angular momentum harmonic coupled to a spin to form a vector (tensor of the first rank). In future calculations we leave A and k as unknown parameters and determine them by fitting to available data.

With the above assumptions the general form of the interaction between the $4f$ electron's moments and the nuclear spin via the conduction electrons at a site of cubic symmetry is written

$$\mathcal{H}_{sp} = \sum_{kpr} \xi(kpr)\,\{[Y^{(k)}(\vec{L}) \times S^{(p)}]^{(r)}_{4f}\}^{\Gamma_4} \times I^{\Gamma_4}\ . \quad (4)$$

The ranks of the orbital operators go from 0 to 4 only, because of our assumptions about the intermediate state not having orbital character greater than $l=2$. The spin rank is either zero or one corresponding to the two types of terms entering the exchange interaction Eq. (1) and the rank r of the coupled orbital and spin operators must be odd to have the proper time symmetry. When the representation $D(r)$ of the group $O(3)$ is decomposed into cubic group representations, only the part that transforms as a time odd Γ_4 vector is retained. The representation Γ_4 is contained once for $r=1,3$ and twice for $r=5$.

The interaction Eq. (4) can be recognized as an invariant under the cubic group and only those parts of the operators referring to the $4f$ electrons that transform under the representation Γ_4 are retained. As shown in Table II there are eight different combinations of k, p, and r that enter the self-polarization Hamiltonian; thus without further assumptions this is the number of parameters needed to describe H_{sp} which is the field acting on the nuclear spin when one takes the expectation values of the $4f$ electron operators in Eq. (4). Most of the parameters $\xi(kpr)$ can be identified with one of the three contributions to the hyperfine interaction Eq. (3), but as seen from Table II there are three parameters which have contributions from both the spin and dipole terms. We could have included in Eq. (4) the direct hyperfine interaction between $4f$ electrons and the nucleus; it would contribute to three terms, $\xi(011)$, $\xi(101)$, and $\xi(211)$. However, as we will eventually be using Eq. (4) to explain the variation of self-polarization field across the rare-earth series, the direct hyperfine interaction from the $4f$ electrons is expressly omitted from this equation.

There is another form of the self-polarization interaction which is more appropriate when we make some assumptions about the nature of the intermediate states. If we focus on conduction electrons with d character (those with s or p character are not split at sites of cubic symmetry and will not alter the conclusions we draw) they will be split by the cubic crystal field of the surroundings. When we neglect this splitting the expression for $\mathcal{H}_{\text{sp}}$ Eq. (4) reduces to an isotropic form like Eq. (3) where the orbital and spin operators are replaced by those referring to the $4f$ electrons. However, if the crystal-field splitting of the d electrons is greater than their spin-orbit coupling, it makes sense to classify the orbital operators referring to the d conduction electrons in Eqs. (1) and (3) according to representations of the cubic group before they are coupled to the spin operators. This scheme of coupling the orbital and spin operators of the d conduction electron reflects itself in the classification of the $4f$ electron's operators in Eq. (1) in order to keep Eq. (1) in an invariant form. Thus in this scheme the hyperfine interactions induced by the $4f$ electrons by their interaction with the conduc-

TABLE II. Parameters entering the general self-polarization hyperfine interaction for cubic symmetry Eq. (4),

$$\mathcal{H}_{\text{sp}}=\sum_{kpr}\xi(kpr)[(Y^k\times S^p)^r_{4f}]^{\Gamma_4}\times I^{\Gamma_4}\ .$$

The tensor of rank r must always be time-odd.

	Parameters $\xi(kpr)$		Possible combinations[a]	
			Hyperfine interaction	Exchange interaction
$r=1$	$k=0$ $p=1$	$\xi(011)$	Spin only H_{01}	Spin only $a_0b_0\vec{S}\cdot\vec{s}$
	$k=1$ $p=0$	$\xi(101)$	Orbit only H_{10}	Orbit only $a_1c_1\vec{L}\cdot\vec{l}$
	$k=2$ $p=1$	$\xi(211)$	Dipole contribution H_{21}	$a_2b_2Y_2^*(\vec{L})\cdot Y_2(\vec{l})\vec{S}\cdot\vec{s}$
$r=3$	$k=2$ $p=1$	$\xi(213)$	Dipole contribution H_{21}	$a_2b_2Y_2^*(\vec{L})\cdot Y_2(\vec{l})\vec{S}\cdot\vec{s}$
	$k=3$ $p=0$	$\xi(303)$	Orbital part H_{10}	$a_3c_3Y_3^*(\vec{L})\cdot Y_3(\vec{l})$
	$k=4$ $p=1$	$\xi(413)$	Spin and dipole $H_{01}+H_{21}$	$a_4b_4Y_4^*(\vec{L})\cdot Y_4(\vec{l})\vec{S}\cdot\vec{s}$
$r=5$	$k=4$ $p=1$	$\xi(415)$	Spin and dipole $H_{01}+H_{21}$	$a_4b_4Y_4^*(\vec{L})\cdot Y_4(\vec{l})\vec{S}\cdot\vec{s}$
	$k=4$ $p=1$	$\xi'(415)$[b]	Spin and dipole $H_{01}+H_{21}$	$a_4b_4Y_4^*(\vec{L})\cdot Y_4(\vec{l})\vec{S}\cdot\vec{s}$

[a] The coefficients a_μ, b_μ, and c_μ refer to the exchange interaction Eq. (1). The coefficients H_{01}, H_{10}, and H_{21} refer to the spin, orbital, and dipole contributions to the hyperfine field, see Eq. (3).

[b] The presence of two parameters $\xi(415)$ and $\xi'(415)$ for $r=5$ comes from the fact that there are two independent representations Γ_4 in the reduction of $D^{(5)}$ in the cubic group.

tion electrons is written

$$\mathcal{H}_{\rm sp}=\sum_{kp\gamma}\xi^{(\gamma)}(kp)\{[Y^k(\vec{L})]^{\Gamma_\gamma}\times S^p]^{\Gamma_4}_{4f}\times I^{\Gamma_4}\ , \tag{5}$$

where the ranks k and p are the same as for Eq. (4) and the representations Γ_γ that can appear are $\gamma=1$, 3, 4, and 5. In Table III we list the nine possibilities. As shown below these nine parameters $\xi^{(\gamma)}(kp)$ are related to the eight parameters $\xi(kpr)$. Each parameter $\xi^{(\gamma)}(kp)$ is associated with a specific contribution from the hyperfine interaction except for $\xi^{(1)}(01)$ which has contributions from both the 6*s* as well as the 5*d* electrons and $\xi^{(1)}(41)$ which has contributions from the spin and dipole terms in Eq. (3).

Although we use the index γ to enumerate the number of parameters $\xi^{(\gamma)}(kp)$, it should be noted that this index has no meaning in the coupling scheme appropriate to the rare-earth electrons, i.e., *LSJ*. Therefore we really have

$$\langle[(Y^k)^{\Gamma_\gamma}\times S^p]^{\Gamma_4}\rangle_{4f}=\sum_r\phi^{(\gamma 4)}(kpr)\,\langle[(Y^k\times S^p)^r]^{\Gamma_4}\rangle_{4f}\ , \tag{6}$$

where the coefficient $\phi^{(\gamma 4)}(kpr)$ is a combination of Clebsch-Gordan coefficients for the cubic and three-dimensional rotation groups

$$\phi^{(\gamma\alpha)}(kpr)\begin{pmatrix}\Gamma_\gamma & \Gamma_p & \Gamma_\alpha\\ j & j' & i\end{pmatrix}\equiv\sqrt{2r+1}\sum_{qq'}(-)^{k-p-q'}(\Gamma_\gamma j\,|kq)\begin{pmatrix}k & p & r\\ q & j' & -q'\end{pmatrix}(rq'|\Gamma_\alpha i)\ . \tag{7}$$

The symbol $(\Gamma_\gamma j\,|kq)$ defined in Eq. (14) gives the linear combination of spherical harmonics Y_{kq} to make up a Kubic harmonic Γ_γ, see Ref. 7. By placing the relation Eq. (6) in Eq. (5) and comparing the ensuing expressions to Eq. (4) we find that

$$\xi(kpr)=\sum_\gamma\xi^{(\gamma)}(kp)\phi^{(\gamma 4)}(kpr)\ . \tag{8}$$

The form Eq. (5) is useful if details of the intermediate (conduction-electron) states are known. For example, if they are not spin-orbit-coupled states the dipolar term does not contribute to $\xi^{(1)}(41)$ and $\xi^{(4)}(41)$, and we have one fewer parameter, i.e., eight. If in addition only 5*d*-t_{2g} states need be considered $\xi^{(3)}(21)=-\xi^{(5)}(21)$ and there are seven independent parameters. Finally, if only 5*d*-e_g states need be considered, only Γ_1 and Γ_3 are possible and we have only four parameters $\xi^{(1)}(01)$, $\xi^{(3)}(21)$, $\xi^{(1)}(41)$, and $\xi^{(3)}(41)$.

To determine the variation of the self-polarization

TABLE III. Parameters entering the general self-polarization hyperfine interaction for cubic symmetry, Eq. (5),

$$\mathcal{H}_{\rm sp}=\sum_{kp\gamma}\xi^{(\gamma)}(kp)[(Y^k)^{\Gamma_\gamma}\times S^p]^{\Gamma_4}_{4f}\times I^{\Gamma_4}\ .$$

The sum of the ranks of the tensors $k+p$ must be odd to satisfy time symmetry.

	Parameters $\xi^{(\gamma)}(kp)$	Contributions from[a] Hyperfine interactions Eq. (3)	Contributions from[a] Exchange interactions Eq. (1)
k γ p			
0 1 1	$\xi^{(1)}(01)$	H_{01}	$a_0b_0\vec{S}\cdot\vec{s}$
1 4 0	$\xi^{(4)}(10)$	H_{10}	$a_1c_1\vec{L}\cdot\vec{l}$
2 3 1	$\xi^{(3)}(21)$	H_{21}	$a_2b_2[Y_2^*(\vec{L})\cdot Y_2(\vec{l})]\vec{S}\cdot\vec{s}$
2 5 1	$\xi^{(5)}(21)$		
3 4 0	$\xi^{(4)}(30)$	H_{10}	$a_3c_3Y_3^*(\vec{L})\cdot Y_3(\vec{l})$
4 1 1	$\xi^{(1)}(41)$	$H_{01}+H_{21}$	$a_4b_4[Y_4^*(\vec{L})\cdot Y_4(\vec{l})]\vec{S}\cdot\vec{s}$
4 3 1	$\xi^{(3)}(41)$	H_{21}	
4 5 1	$\xi^{(5)}(41)$		
4 4 1	$\xi^{(4)}(41)$		

[a] The coefficients a_μ, b_μ, and c_μ refer to the exchange interaction Eq. (1). The coefficients H_{01}, H_{10}, and H_{21} refer to the spin, orbital, and dipole contributions to the hyperfine field, see Eq. (3).

field across the rare-earth series it is necessary to evaluate the average the $4f$ electron operators entering Eq. (4) over the appropriate crystal- and molecular-field states. This is done in four steps.

(1) The n $4f$ electron operators are projected on the ground state given by Hund's rule in the Russell-Saunders coupling scheme.

$$\sum_{i=1}^{n} Y_{\mu\nu}(\vec{1}_i) \equiv c_\mu Y_{\mu\nu}(\vec{L}) \tag{9a}$$

and

$$\sum_{i=1}^{n} Y_{\mu\nu}(\vec{1}_i)\vec{s}_i \equiv b_\mu Y_{\mu\nu}(\vec{L})\vec{S} \ . \tag{9b}$$

The values for b_μ and c_μ are given in Table I. Some of these have been given previously.

(2) The orbital and spin operators are projected onto the total angular momentum manifold J of the ground state.

$$Y_\mu(\vec{L}) = d_\mu(J)\,Y_\mu(\vec{J}) \ , \tag{10a}$$

where

$$d_\mu(J) = \frac{\langle LSJ \,\|\, Y_\mu(\vec{L}) \,\|\, LSJ\rangle}{\langle J \,\|\, Y_\mu \,\|\, J\rangle} = (-1)^{L+S+J+\mu}(2J+1)\begin{Bmatrix} J & J & \mu \\ L & L & S \end{Bmatrix} \tag{10b}$$

and the curly bracket represents a $6j$ symbol. In Table IV we list the values for d_1, d_2, and d_3. For the spin-dependent terms we find

$$[Y_{\mu\nu}(\vec{L}) \times S_q^1]_m^r = \langle \mu\nu 1 q \,|\, \mu 1 r m\rangle M_{\mu 1}^r(J)\,Y_{rm}(\vec{J}) \ , \tag{11a}$$

where the term in angular brackets is a Clebsch-Gordan (vector coupling) coefficient, and

$$M_{\mu 1}^r(J) = (2J+1)\sqrt{2\mu+1}\sqrt{3}\begin{Bmatrix} L & L & \mu \\ S & S & 1 \\ J & J & r \end{Bmatrix} \ . \tag{11b}$$

The curly bracket represents a $9j$ symbol. From the definition of the irreducible tensors, Eq. (2) we have

$$S_z = [S(S+1)(2S+1)/3]^{1/2} S_0^1 \tag{12}$$

and

$$\frac{1}{\sqrt{2}} S_\pm = \mp [S(S+1)(2S+1)/3]^{1/2} S_{\pm 1}^1 \ .$$

TABLE IV. Projection factors defined by Eqs. (10b) and (10c).

	d_1	d_2	d_3
Ce^{3+}	0.9035	0.8571	0.7825
Pr^{3+}	0.8863	0.8497	0.7948
Nd^{3+}	0.8569	0.8170	0.7583
Pm^{3+}	0.8038	0.7488	0.6698
Sm^{3+}	0.6838	0.5811	0.4438
Eu^{3+}	0	0	0
Gd^{3+}			
Tb^{3+}	1.2748	1.1095	0.8876
Dy^{3+}	1.1721	1.1058	1.0106
Ho^{3+}	1.1229	1.0823	1.0227
Er^{3+}	1.0934	1.0617	1.0148
Tm^{3+}	1.0719	1.0415	0.9959
Yb^{3+}	1.0498	1.0102	0.9476

Therefore when we recouple the orbital and spin operators $S_\alpha \equiv (\mp 1/\sqrt{2})S_\pm, S_z$ by using the above definition we find,

$$[Y_{\mu\nu}(\vec{L}) \times S_\alpha]_m^r \equiv N_{\mu 1}^r(J)\,Y_m^r(\vec{J}) \ ,$$

where

$$N_{\mu 1}^r(J) = [S(S+1)(2S+1)/3]^{1/2} M_{\mu 1}^r(J) \ . \tag{13a}$$

In Table V we list the values of those recoupling coefficients which will be needed for the expressions in Sec. III. The recoupling coefficients d_1 and N_{01}^1 can be expressed in terms of the Landé g_J factor.

$$d_1 = \left[\frac{J(J+1)(2J+1)}{L(L+1)(2L+1)}\right]^{1/2}(2-g_J) \tag{10c}$$

and

$$N_{01}^1 = \left[\frac{J(J+1)(2J+1)}{3(2L+1)}\right]^{1/2}(g_J-1) \ . \tag{13b}$$

(3) We determine the proper linear combinations of spherical harmonics that make up the Kubic harmonics Γ_4

$$[Y^r(\vec{J})]_i^{\Gamma_4} = \sum_m (\Gamma_4 i \,|\, rm)\,Y_m^r(\vec{J}) \ . \tag{14}$$

Apart from a normalization factor the coefficients $(\Gamma_4 i \,|\, rm)$ have been given by Watanabe for the values of $r = 1$, 3, and 5 we need.[7] In Table VI we list some of the Kubic harmonics needed to study the self-polarization field. In case there is more than one J state to consider, e.g., $SmAl_2$ we write

$$[(Y_\mu(\vec{L}) \times S^p)^r]_i^{\Gamma_4} = \sum_m (\Gamma_4 i \,|\, rm)[Y_\mu(\vec{L}) \times S^p]_m^r = \sum_{\substack{m \\ \nu q}} (\Gamma_4 i \,|\, rm)(-1)^{\mu+p-m}\sqrt{2r+1}\begin{pmatrix} \mu & p & r \\ \nu & q & -m \end{pmatrix} Y_{\mu\nu}(\vec{L})S_q^p \ , \tag{14a}$$

TABLE V. Projection factors defined by Eqs. (13a) and (13b).

	N^0_{11}	N^1_{01}	N^1_{21}	N^2_{11}	N^3_{21}	N^3_{41}	N^5_{41}
Ce^{3+}	0.5345	−0.2259	0.4949	−0.2020	−0.1620	0.5663	−0.0681
Pr^{3+}	0.9909	−0.4671	0.8697	−0.4471	−0.3933	0.8795	−0.2600
Nd^{3+}	1.4210	−0.6870	1.2255	−0.6637	−0.5887	1.1818	−0.3984
Pm^{3+}	1.7974	−0.8593	1.5329	−0.8111	−0.6933	1.3916	−0.4514
Sm^{3+}	2.0226	−0.9009	1.6775	−0.7645	−0.5491	1.2278	−0.1477
Eu^{3+}	1.3093	0	0	0	0	0	0
Gd^{3+}		6.4807					
Tb^{3+}	−3.5406	2.5495	−2.3274	2.8244	2.7563	−1.0512	1.9329
Dy^{3+}	−2.7524	1.8532	−1.9907	2.1013	2.1879	−1.3046	2.0755
Ho^{3+}	−2.1174	1.4005	−1.5703	1.5986	1.6937	−1.1250	1.7266
Er^{3+}	−1.5407	1.0228	−1.1468	1.1762	1.2604	−0.8372	1.3319
Tm^{3+}	−0.9924	0.6779	−0.7282	0.7917	0.8624	−0.5143	0.9455
Yb^{3+}	−0.4629	0.3499	−0.3194	0.4286	0.4904	−0.1870	0.6015

TABLE VI. The Kubic harmonics for Eqs. (22), (23), and (24d) in terms of spherical harmonics quantized along the three principal directions of a cube.

$(Y_k)_j^{\Gamma_\gamma}$	$\sum_q (\Gamma_\gamma j \mid kq) Y_{kq}$
$(Y_1)_z^{\Gamma_4}$	
[100]	Y_{10}
[111]	
[110]	
$(Y_3)_z^{\Gamma_4}$	
[100]	Y_{30}
[111]	$-(2/3)[Y_{30}+(\sqrt{10}/4)(Y_{33}-Y_{3-3})]$
[110]	$-(1/4)[Y_{30}-\sqrt{15/2}(Y_{32}+Y_{3-2})]$
$(Y_4)_z^{\Gamma_1}$	
[100]	$\sqrt{7/12}[Y_{40}+\sqrt{5/14}(Y_{44}+Y_{4-4})]$
[111]	$-(2/3)\sqrt{7/12}[Y_{40}+\sqrt{10/7}(Y_{43}-Y_{4-3})]$
[110]	$-(1/4)\sqrt{7/12}[Y_{40}-\sqrt{10}(Y_{42}+Y_{4-2})-3\sqrt{5/14}(Y_{44}+Y_{4-4})]$
$(Y_5)_z^{\Gamma_4+\Gamma_4'}$	
[100]	$Y_{50}+(3/\sqrt{70})(Y_{54}+Y_{5-4})$
[111]	$-(2/3)[Y_{50}+(8/\sqrt{70})(Y_{53}-Y_{5-3})]$
[110]	$-(1/4)[Y_{50}-\sqrt{42/5}(Y_{52}+Y_{5-2})-(9/\sqrt{70})(Y_{54}+Y_{5-4})]$

where we have used the $3j$ symbol to decompose the product of orbital and spin operators.

(4) Finally the operators $Y_m^r(\vec{J})$ or $[Y_\mu \times S^p]_m^r$ are projected onto the eigenstates of the $4f$ electrons $\langle Y_m^r(\vec{J})\rangle_{4f}$. To determine the states in the magnetically ordered phase of the compounds one must take into account the molecular field acting on the $4f$ electrons in addition to the crystal field. If more than the ground state is occupied the thermal average of the operator over the occupied states must be taken. Details of the wave function for the occupied states of the $4f^n$ electrons for several rare earths have been obtained by Bourcherle and Schweizer from their determination of the $4f$ electron contribution to the magnetic form factor.[1] In those cases where this data is not available from experiment, it is necessary to determine the $4f$ electron states by simultaneously diagonalizing the crystal- and molecular-field Hamiltonians, and then taking the average over thermally occupied states.

If we assume the parameters $\xi(kpr)$ or $\xi^\gamma(kp)$ do not vary across the rare-earth series, and following the above steps we are able to use Eqs. (4) and (5) to determine the self-polarization fields (the expectation value of $\mathcal{H}_{\text{sp}}$ over the $4f$ electron states) for all the rare earths. Needless to say there are too many parameters in general (eight or nine) and we are forced to make further assumptions to obtain a tractable expression. In Sec. III we describe three model calculations which reduce the number of parameters considerably. The ensuing expressions contain fewer parameters, but the assumptions are restrictive and reduce the general applicability of the expressions.

We can also use the above arguments to determine the number of parameters needed to describe the contribution to the magnetization from conduction electrons. The Zeeman interaction between an external field and the conduction electrons is

$$\mathcal{H}_{\text{mag}} = -\vec{\mathrm{m}}_{\text{cond}} \cdot \vec{\mathrm{H}} = -m_{\text{cond}}^{\Gamma_4} \times H^{\Gamma_4} \quad . \tag{15}$$

As m_{cond} represents the magnetic moment induced in the conduction electrons by their interaction with the $4f$ electrons we can write

$$m_{\text{cond}}^{\Gamma_4} = \sum_{kpr} \xi^m(kpr)[(Y^k \times S^p)^r]_{4f}^{\Gamma_4} \quad . \tag{15a}$$

These are all the possible combinations of $4f$ electron operators that transform as the Γ_4 representation of the cubic group and are time-odd. Thus from symmetry alone the same *number* of parameters ξ enter the general expressions for the contributions to the magnetization from the conduction electrons as for the self-polarization field. Note that if conduction electrons with different orbital characters, i.e., *spd*, are present, they contribute to $\xi^m(kpr)$ but do not produce additional parameters. Thus the most general expression for the magnetization of the conduction electrons is given by the eight parameters $\xi^m(kpr)$ or the nine parameters $\xi_m^{(\gamma)}(kp)$ and these parameters describe the variation of the conduction-electron contribution to the magnetization across the rare-earth series. If details of the conduction electrons are known or assumed, we can use Eq. (1) to directly find the number of parameters that enter Eq. (15). By using the explicit interaction Eq. (1) we drastically reduce the number of unknowns, however we must have details of the conduction-electron structure.

III. MODEL CALCULATIONS

As we saw in Sec. II there are a large number of parameters that enter the general expressions for the hyperfine field and orbital and spin polarizations of the conduction electrons. To arrive at a tractable analysis of the experimental data it is necessary to reduce the number of parameters. Therefore we must resort to specific models of the conduction electrons and of the rare-earth conduction-electron interactions.

In the following calculations we make the following approximations:

(i) The conduction electrons of interest are of $5d$ and $6s$ character. The $6s$ electrons have only spin polarization while the $5d$ have orbital and spin contributions. We further assume there is negligible overlap between $5d$ electrons localized at different rare-earth sites (tight-binding approximation). The $5d$ electron does strongly interact with other conduction electrons and forms a virtual-bound state (vbs). As there is usually less than one $5d$ electron per rare earth, we further neglect the intra-atomic Coulomb interactions U and J between d electrons.

(ii) The rare-earth $5d$ conduction-electron interaction is described by the $4f$-$5d$ intra-atomic Coulomb interaction. The integrals entering the interaction could be evaluated from the $4f$-$5d$ Slater atomic integrals F_k and G_k. We will use these atomic integrals only to determine the ratios of the higher-rank interactions with respect to the bilinear interaction. This allows us to determine these interactions by fitting them to the data with only one exchange parameter. For the $4f$-$6s$ interaction we have one parameter which is determined by fitting to the data.

(iii) The polarization of the conduction electrons by the rare-earth $4f$ moments is calculated by using linear-response theory. This method was originally used by Caroli, Caroli, and Fredkin,[8] then by Dworin and Narath,[9] and most recently by Huang-Liu, Ling, and Orbach.[6] In previous calculations the $5d$ vbs was polarized by the Zeeman interaction and the intra-atomic interaction between $5d$ electrons were taken into account, i.e., the Coulomb direct and exchange interactions represented, respectively, by the integrals U and J. In our application we neglect U and J and the $5d$ vbs is polarized by its interaction with the rare-earth $4f$ electron's moments which themselves are polarized in the magnetically ordered states of the compounds under consideration.

(iv) We consider separately the effects of crystalline field and spin-orbit coupling on the $5d$ vbs, and the splitting of the $5d$ vbs and $6s$ states into spin-up–spin-down bands. In reality all three effects occur, however the lack of detailed knowledge of the nature of the conduction electrons does not permit us to simultaneously take them into account. When we split the conduction electrons into two spin bands we implicitly break time-reversal symmetry. The results derived in Sec. II were based on the assumption that time-reversal symmetry is preserved. Therefore terms not present in Eqs. (4) and (5) will appear when we consider the splitting of the conduction electrons into spin-up and spin-down bands.

On the basis of the above assumptions we find the contribution of conduction electrons to the hyperfine field, i.e., the self-polarization field, by calculating the expectation values of the operators entering Eq. (3) for $5d$ and $6s$ electrons,

$$H_{\text{sp}} = A\,\{\langle l_z\rangle_d + \sqrt{20/7}\,\langle [Y_2(\vec{l}\,)\times\vec{s}\,]^1_0\rangle_d\} + B\,\langle s_z\rangle_d + C\,\langle s_z\rangle_s \;. \tag{16}$$

Thus the calculation of H_{sp} reduces to one of finding the orbital and spin polarizations of the conduction electrons and the expectation value of the dipole term $[Y_2(\vec{l}\,)\times\vec{s}\,]^1$. Thus in this approach we find the contribution of the conduction electrons to the magnetization as well as to the hyperfine field

$$M_{\text{cond}} \equiv \mu_B[\langle l_z\rangle_d + 2(\langle s_z\rangle_d + \langle s_z\rangle_s)] \;. \tag{17}$$

In Eqs. (16) and (17) only the components of the conduction-electron operators parallel to the internal molecular field appear; the other components are either zero or very small and may safely be neglected. The average for the s electron $\langle s_z\rangle_s$ is straightforward and is written in our notation as

$$\langle s_z\rangle_s = a_0' b_0 N^1_{01}\,\langle Y_{10}(J)\rangle_{4f}\chi_s \;, \tag{18}$$

where a_0' is the isotropic $4f$-$6s$ exchange constant and χ_s the susceptibility of the $6s$ electrons.

To calculate the d electron averages entering Eqs. (16) and (17) we use linear-response theory. The expectation values $\langle l_z\rangle_d$, $\langle s_z\rangle_d$, and $\langle [Y_2(\vec{l}\,)\times\vec{s}\,]^1_0\rangle_d$ are the response of the conduction electrons due to the "perturbation" of the $4f$-$5d$ exchange interaction, Eq. (1), i.e., if we write the Hamiltonian for the conduction electron as

$$\mathcal{H} = \mathcal{H}_0 - AF \;, \tag{19}$$

where A is a conduction-electron operator which couples to a field F, then to first order in F, the response associated with *another* conduction-electron operator B is given as

$$\begin{gathered}\langle B\rangle - \langle B\rangle_{F=0} = \chi_{BA}F \;, \\ \chi_{BA} = \sum_{n_1 n_2} \langle n_1|B|n_2\rangle\langle n_2|A|n_1\rangle S(n_1 n_2) \;.\end{gathered} \tag{19a}$$

The states $|n\rangle$ are eigenstates of the unperturbed Hamiltonian $\mathcal{H}_0$ and $S(n_1 n_2)$ is the susceptibility which can in principle be calculated if enough is known about the states and spectrum of $\mathcal{H}_0$, but which we will consider as unknown in our work and will assume to remain constant as we go across the rare-earth series. The operator A for our calculation are those terms in Eq. (1) referring to the conduction electrons, i.e., $Y_{\mu\nu}(\vec{l}\,)$ and $Y_{\mu\nu}(\vec{l}\,)\vec{s}$, and the field F is the remainder in Eq. (1) after one takes the expectation values of the rare-earth $4f$ electron operators over the appropriate crystal- and molecular-field states. That is to say we write in our case

$$-AF \equiv \mathcal{H}_{\langle 4f\rangle-5d} = -2\sum_{\mu=0}^{4}\sum_{\nu=-\mu}^{\mu}(-)^{\nu}a_\mu b_\mu Y_{\mu\nu}(\vec{l}\,)\vec{s}\cdot\langle Y_{\mu-\nu}(\vec{L})\vec{S}\rangle_{4f} - \tfrac{1}{2}\sum_{\mu=0}^{4}c_\mu\sum_{\nu=-\mu}^{\mu}(-)^{\nu}Y_{\mu\nu}(\vec{l}\,)\langle Y_{\mu-\nu}(\vec{L})\rangle_{4f} \;. \tag{20}$$

Finally the operators B are those for which we want to find the expectation values, i.e., $\langle l_z\rangle_d$, $\langle s_z\rangle_d$, and $\langle [Y_2(\vec{l}\,)\times\vec{s}\,]^1_0\rangle_d$. In summary we can rewrite Eq. (19a) as

$$\langle B_z\rangle_{5d} = -\sum_{n_1 n_2}\langle n_1|B_z|n_2\rangle\langle n_2|\mathcal{H}_{\langle 4f\rangle 5d}|n_1\rangle S(n_1 n_2) \;, \tag{19b}$$

when we set to zero the expectation values of the operators in the *absence* of the $4f$-$5d$ exchange interaction, and the components of the vector operator B perpendicular to the molecular field.

Now we evaluate the expectation values by using Eq. (19b) in three different limits for the unperturbed Hamiltonian $\mathcal{H}_0$. First when the crystal-field splitting of the $5d$ electrons is most important, second when the $5d$ band is split into spin-up and spin-down bands, and third when spin-orbit coupling is important so we have two bands with $j=\frac{3}{2}$ and $\frac{5}{2}$. In each case we have three susceptibilities $S(n_1 n_2)$ but their meanings are different as they refer to different limits of the eigenstates of the conduction-electron Hamiltonian $\mathcal{H}_0$.

A. Strong crystal-field limit

In this case the eigenstates of the $5d$ electrons are labeled by the cubic group representations e_g and t_{2g} and the spin. As we neglect the spin polarization of the band and the spin-orbit coupling, the susceptibility depends on the orbital labels e_g and t_{2g}, and Eq. (19b) is written

$$\langle B_z\rangle = -\sum_{\phi_1\phi_2}\sum_{m_1m_2}\langle\phi_1 m_1|B_z|\phi_2 m_2\rangle\langle\phi_2 m_2|\mathcal{H}_{\langle 4f\rangle 5d}|\phi_1 m_1\rangle S(\phi_1\phi_2) \;, \tag{21}$$

where the ϕ's are the $5d-e_g$ and t_{2g} orbitals and m refers to the $5d$ spin. If one resorts to the details of the virtual-bound-state model, one can write the susceptibilities $S(\phi_1\phi_2)$ in terms of the energies and linewidths of the t_{2g} and e_g states, see Ref. 6. By placing the $4f$-$5d$ exchange interaction Eq. (20) in Eq. (21) we find[10]

$$\langle l_z\rangle_d = \frac{2}{\sqrt{10}}a_1c_1\langle[Y_1(\vec{L})]_z^{\Gamma_4}\rangle[S(tt)+4S(te)] - \frac{4}{\sqrt{10}}a_3c_3\langle[Y_3(\vec{L})]_z^{\Gamma_4}\rangle[S(tt)-S(te)] \;, \tag{22}$$

$$\langle s_z\rangle_d = \frac{a_0b_0}{\sqrt{5}}\langle Y_0(\vec{L})S_z\rangle[3S(tt)+2S(ee)] - \sqrt{6/5}\,a_4b_4\langle(Y_4)^{\Gamma_1}S_z\rangle[S(tt)-S(ee)] \;. \tag{23}$$

We have classified the $4f$ electron orbital operators according to the cubic group representations.[7] The axis of quantization z is along the direction of the molecular field. As this direction varies from one rare-earth compound to another we give in Table VI the explicit forms of the operators in terms of the spherical harmonics referred to the three principal cubic axis, i.e., [100], [110], and [111].

For the dipole term it is not possible to give one expression, as Eqs. (22) and (23), valid for all principal axes and we must give a separate expression for each principal direction. For the molecular field along [100] we find

$$\begin{aligned}
&\langle[Y_2(\vec{l})\times\vec{s}]_0^1\rangle_d \\
&\quad= -\tfrac{1}{7}\sqrt{2/5}\,a_2b_2\{\langle Y_{20}(\vec{L})S_z\rangle[3S(tt)+4S(ee)] - \tfrac{1}{2}\sqrt{3/2}\langle[Y_{21}(\vec{L})S_- - Y_{2-1}(\vec{L})S_+]\rangle[3S(tt)+4S(te)]\} \\
&\qquad -\tfrac{1}{7}\sqrt{2}\,a_4b_4\Big\{\langle\{Y_{40}(\vec{L})-\sqrt{7/10}[Y_{44}(\vec{L})+Y_{4-4}(\vec{L})]\}S_z\rangle[S(tt)-S(ee)] \\
&\qquad\qquad -\frac{3}{4\sqrt{5}}\langle\{[Y_{41}(\vec{L})-\sqrt{7}\,Y_{4-3}(\vec{L})]S_- + \text{c.c.}\}\rangle[S(tt)-S(te)]\Big\} \;.
\end{aligned} \tag{24a}$$

For [111] we find

$$\begin{aligned}
\langle[Y_2(\vec{l})\times\vec{s}]_0^1\rangle_d = {}& -\tfrac{1}{7}\sqrt{2/5}\,a_2b_2\Big\{\langle Y_{20}(\vec{L})S_z\rangle[3S(tt)+4S(te)] - \frac{1}{2\sqrt{6}}\langle Y_{21}(\vec{L})S_- - Y_{2-1}(\vec{L})S_+\rangle \\
&\qquad \times[9S(tt)+4S(te)+8S(ee)] - \frac{2}{\sqrt{3}}\langle Y_{22}(\vec{L})S_+ + Y_{2-2}(\vec{L})S_-\rangle[S(te)-S(ee)]\Big\} \\
&+\tfrac{1}{21}\sqrt{2}\,a_4b_4\Big\{4\langle\{Y_{40}(\vec{L})-\tfrac{1}{2}\sqrt{7/10}[Y_{43}(\vec{L})-Y_{4-3}(\vec{L})]\}S_z\rangle[S(tt)-S(te)] \\
&\qquad +\frac{1}{2\sqrt{5}}\langle Y_{41}(\vec{L})S_- - Y_{4-1}(\vec{L})S_+\rangle[S(tt)-5S(te)+4S(ee)] \\
&\qquad +\frac{1}{2\sqrt{5}}\langle Y_{42}(\vec{L})S_+ + Y_{4-2}(\vec{L})S_-\rangle[-7S(tt)+8S(ee)-S(te)] \\
&\qquad +\sqrt{7/5}\langle Y_{44}(\vec{L})S_- + Y_{4-4}(\vec{L})S_+\rangle[-2S(tt)+S(te)+S(ee)]\Big\} \;.
\end{aligned} \tag{24b}$$

Finally for [110] we find

$$\begin{aligned}\langle [Y_2(\vec{l}) \times \vec{s}\,]_0^1\rangle_d = &-\tfrac{1}{7}\sqrt{2/5}\,a_2b_2\{\langle Y_{20}(\vec{L})S_z\rangle[3S(tt)+3S(te)+S(ee)]\\ &-\tfrac{1}{2}\sqrt{3/2}\langle Y_{21}(\vec{L})S_- - Y_{2-1}(\vec{L})S_+\rangle[3S(tt)+2S(te)+2S(ee)]\\ &+\sqrt{3/2}\langle Y_{2-1}(\vec{L})S_- - Y_{21}(\vec{L})S_+ + [Y_{22}(\vec{L})+Y_{2-2}(\vec{L})]S_z\rangle[S(ee)-S(te)]\}\\ &-\frac{\sqrt{2}}{56}a_4b_4\Bigg(\langle Y_{40}(\vec{L})S_z\rangle[S(tt)-6S(te)+5S(ee)]+\frac{3}{2\sqrt{5}}\langle Y_{41}(\vec{L})S_- - Y_{4-1}(\vec{L})S_+\rangle\\ &\qquad\times[3S(tt)-5S(te)+2S(ee)]\\ &+\frac{3}{2\sqrt{5}}\langle Y_{4-1}(\vec{L})S_- - Y_{41}(\vec{L})S_+\rangle[7S(tt)-5S(te)-2S(ee)]\\ &+\sqrt{2/5}\langle[Y_{42}(\vec{L})+Y_{4-2}(\vec{L})]S_z\rangle[7S(tt)-6S(te)-S(ee)]\\ &+\tfrac{3}{2}\sqrt{7/5}\langle Y_{43}(\vec{L})S_- - Y_{4-3}(\vec{L})S_+\rangle[-3S(tt)+S(te)+2S(ee)]\\ &+\tfrac{3}{2}\sqrt{7/5}\langle Y_{4-3}(\vec{L})S_- - Y_{43}(\vec{L})S_+\rangle[S(tt)+S(te)-2S(ee)]\\ &+3\sqrt{7/10}\langle[Y_{44}(\vec{L})+Y_{4-4}(\vec{L})]S_z\rangle[-3S(tt)+2S(te)+S(ee)]\Bigg|\ .\end{aligned}\tag{24c}$$

For most rare earths we can confine our attention to one J manifold and write the orbital and spin operators in terms of total angular momentum operators. By using Eqs. (10) and (13), and remembering we only want the "time-odd" terms that transform according to the Γ_4 representation, see Eq. (5), we find[10]

$$\langle l_z\rangle_d = \frac{2}{\sqrt{10}}a_1c_1d_1\langle[Y_1(\vec{J})]_z^{\Gamma_4}\rangle[S(tt)+4S(te)] - \frac{4}{\sqrt{10}}a_3c_3d_3\langle[Y_3(\vec{J})]_z^{\Gamma_4}\rangle[S(tt)-S(te)]\ , \tag{22a}$$

$$\begin{aligned}\langle s_z\rangle_d = &\frac{1}{\sqrt{5}}a_0b_0N_{01}^1\,\langle[Y_1(\vec{J})]_z^{\Gamma_4}\rangle[3S(tt)+2S(ee)]\\ &+\tfrac{1}{3}\sqrt{7/10}\,a_4b_4\langle\{2N_{41}^3\,[Y_3(\vec{J})]_z^{\Gamma_4} - \sqrt{5}N_{41}^5\,[Y_5(\vec{J})]_z^{\Gamma_4+\Gamma_4'}\}\rangle[S(tt)-S(ee)]\ ,\end{aligned}\tag{23a}$$

and

$$\begin{aligned}\langle [Y_2(\vec{l}) \times \vec{s}\,]_0^1\rangle_d = &\tfrac{1}{35}a_2b_2N_{21}^1\,\langle[Y_1(\vec{J})]_z^{\Gamma_4}\rangle[15S(tt)+12S(te)+8S(ee)]\\ &+\frac{4\sqrt{6}}{35}a_2b_2N_{21}^3\,\langle[Y_3(\vec{J})]_z^{\Gamma_4}\rangle[S(te)-S(ee)]\\ &+\frac{1}{21\sqrt{2}}a_4b_4N_{41}^3\,\langle[Y_3(\vec{J})]_z^{\Gamma_4}\rangle[7S(tt)-3S(te)-4S(ee)]\\ &-\tfrac{1}{21}\sqrt{2/5}\,a_4b_4N_{41}^5\,\sum_m A_m(S(ij))\langle Y_{5m}(\vec{J})+Y_{5-m}(\vec{J})\rangle\ .\end{aligned}\tag{24d}$$

In Table VI we list the Kubic harmonics $[Y_k(\vec{J})]_z^{\Gamma_4}$ in terms of the spherical harmonics for z along the three principal cubic axes. When the representation $D^{(5)}$ is decomposed in terms of the cubic group the representation Γ_4 appears twice; for this reason we have two different representations for $[Y_5(\vec{J})]_z^{\Gamma_4}$, and the specific combination in Eq. (23a) cannot be found from symmetry alone. The combinations given in Table VI have been found to be the appropriate ones from our calculations. In addition in Eq. (24d) the harmonics $Y_5(\vec{J})$ come from different parts of Eqs. (24) and it is further not possible to write down one combination of susceptibilities associated with the harmonics $Y_5(\vec{J})$ that applies to all three principal cubic direction. For this reason we give them explicitly for each direction. For [100] we find

$$\sum_m A_m(S(ij))\langle Y_{5m}(\vec{J})+Y_{5-m}(\vec{J})\rangle=[2S(tt)+3S(te)-5S(ee)]\langle Y_{50}(\vec{J})\rangle$$
$$+3\sqrt{7/10}[2S(tt)-3S(te)+S(ee)]\langle Y_{54}(\vec{J})+Y_{5-4}(\vec{J})\rangle\ , \tag{25a}$$

for [111] we find

$$\sum_m A_m(S(ij))\langle Y_{5m}(\vec{J})+Y_{5-m}(\vec{J})\rangle=-\tfrac{2}{3}\{[11S(tt)-15S(te)+4S(ee)]\langle Y_{50}(\vec{J})\rangle$$
$$+\sqrt{7/10}[S(tt)+6S(te)-7S(ee)]\langle Y_{53}(\vec{J})-Y_{5-3}(\vec{J})\rangle\}\ , \tag{25b}$$

and for [110] we find

$$\sum_m A_m(S(ij))\langle Y_{5m}(\vec{J})+Y_{5-m}(\vec{J})\rangle=\tfrac{1}{8}[23S(tt)-60S(te)+37S(ee)]\langle Y_{50}(\vec{J})\rangle$$
$$+\tfrac{1}{4}\sqrt{21/10}[13S(tt)-12S(te)-S(ee)]\langle Y_{52}(\vec{J})+Y_{5-2}(\vec{J})\rangle$$
$$+\tfrac{9}{8}\sqrt{7/10}[-S(tt)+4S(te)-3S(ee)]\langle Y_{54}(\vec{J})+Y_{5-4}(\vec{J})\rangle\ . \tag{25c}$$

When we make the simplifying assumption that the susceptibilities do not depend on the crystal-field level, i.e.,

$$S(tt)=S(te)=S(ee)\equiv\mathcal{S}\ ,$$

we find from Eqs. (22)–(24)

$$\langle l_z\rangle_d=\sqrt{10}a_1c_1\mathcal{S}\langle Y_{10}(\vec{L})\rangle=\frac{5}{\sqrt{70}}a_1\mathcal{S}\langle L_z\rangle_{4f}\ ,\quad \langle s_z\rangle_d=\sqrt{5}a_0b_0\mathcal{S}\langle Y_0(\vec{L})S_z\rangle=\sqrt{5/7}a_0\mathcal{S}\langle S_z\rangle_{4f}\ .$$

and

$$\langle[Y_2(\vec{l})\times\vec{s}]_0^1\rangle_d=-\sqrt{2/5}a_2b_2\mathcal{S}\langle\{Y_{20}(\vec{L})S_z-\tfrac{1}{2}\sqrt{3/2}[Y_{21}(\vec{L})S_--Y_{2-1}(\vec{L})S_+]\}\rangle_{4f}=a_2b_2\mathcal{S}\langle[Y_2(\vec{L})\times\vec{s}]_0^1\rangle_{4f}\ . \tag{26}$$

In this limit we find the same results as those found by using isotropic exchange. The effect of the crystal-field splitting can be seen by comparing Eqs. (22)–(24) to Eqs. (26). It makes the $5d$ electron expectation values dependent on higher powers of the $4f$-$5d$ exchange interaction.

B. Spin-split bands

Below the magnetic ordering temperature it is conceivable that the conduction electrons are separated into two bands, one with predominantly spin up, the other spin down.[11] If one assumes the susceptibilities $S(n_1n_2)$ depend only on the spin indices and not the orbital variables, the expectation value for the conduction-electron operators, Eq. (19b), is

$$\langle B_z\rangle_d=-\sum_{\substack{m_1\sigma_1\\ m_2\sigma_2}}\langle m_1\sigma_1|B_z|m_2\sigma_2\rangle\langle m_2\sigma_2|\mathcal{H}_{(4f)5d}|m_1\sigma_1\rangle S(\sigma_1\sigma_2)\ . \tag{27}$$

Here m labels the $5d$ orbital variables and σ the spin. There are three different susceptibilities S_{++}, S_{--}, and S_{+-}. When we place the $4f$-$5d$ exchange interaction Eq. (20) in this expression we find,

$$\langle l_z\rangle_d=\sqrt{5/2}a_1c_1\langle Y_{10}(\vec{L})\rangle\left[\sum_\sigma S_{\sigma\sigma}\right]+2\sqrt{10}a_1b_1\langle Y_{10}(\vec{L})S_z\rangle\left[\sum_\sigma\sigma S_{\sigma\sigma}\right]$$
$$=\sqrt{5/2}a_1c_1d_1\langle Y_{10}(\vec{J})\rangle(S_{++}+S_{--})+\sqrt{10/3}a_1b_1\left[-\frac{1}{\sqrt{2J+1}}N_{11}^{0}+\sqrt{2}N_{11}^{2}\langle Y_{20}(\vec{J})\rangle\right](S_{++}-S_{--})\ , \tag{28}$$

$$\langle s_z\rangle_d=\frac{1}{2}\left[\frac{5}{2L+1}\right]^{1/2}a_0c_0\left[\sum_\sigma\sigma S_{\sigma\sigma}\right]+\frac{\sqrt{5}}{2}a_0b_0\langle Y_0(\vec{L})S_z\rangle\left[\sum_\sigma S_{\sigma\sigma}\right]$$
$$=\frac{1}{4}\left[\frac{5}{2L+1}\right]^{1/2}a_0c_0(S_{++}-S_{--})+\frac{\sqrt{5}}{2}a_0b_0N_{01}^{1}\langle Y_{10}(\vec{J})\rangle(S_{++}+S_{--})\ , \tag{29}$$

and

$$\langle [Y_2(\vec{l}) \times \vec{s}]^1_0 \rangle_d = \frac{a_2}{\sqrt{10}} \left[-c_2 \langle Y_{20}(\vec{L}) \rangle \left[\sum_\sigma \sigma S_{\sigma\sigma} \right] - b_2 \langle Y_{20}(\vec{L}) S_z \rangle \left[\sum_\sigma S_{\sigma\sigma} \right] + \sqrt{3/2}\, b_2 \langle Y_{21}(\vec{L}) S_- - Y_{2-1}(\vec{L}) S_+ \rangle S_{+-} \right]$$

$$= \frac{a_2}{5\sqrt{2}} \left(\sqrt{2} b_2 N^1_{21} \langle Y_{10}(\vec{J}) \rangle (S_{++} + S_{--} + 3S_{+-}) - \sqrt{3} b_2 N^3_{21} \langle Y_{30}(\vec{J}) \rangle (S_{++} + S_{--} - 2S_{+-}) \right.$$

$$\left. - \frac{\sqrt{5}}{2} c_2 d_2 \langle Y_{20}(\vec{J}) \rangle (S_{++} - S_{--}) \right) . \tag{30}$$

The difference in the susceptibilities $S_{\sigma\sigma'}$ depends on the spin polarization of the conduction bands. It disappears as one approaches the magnetic ordering temperature and reaches a maximum at low temperatures. If one makes the assumption that the various susceptibilities are equal we find Eqs. (28)–(30) reduce to Eqs. (26).

The 6*s* conduction band will also be spin polarized and a splitting into spin-up and spin-down bands also develops. When one takes this into account for these electrons one finds,

$$\langle s_z \rangle_s = \tfrac{1}{2} a_0' \left(\frac{c_0}{2\sqrt{2L+1}} (S'_{++} - S'_{--}) + b_0 N^1_{01} \langle Y_{10}(\vec{J}) \rangle (S'_{++} + S'_{--}) \right) , \tag{31}$$

where a_0' denotes the isotropic 4*f*-6*s* exchange constant and $S'_{\sigma\sigma}$ the susceptibilities for the 6*s* bands. If one takes the spin splitting of the 6*s* band into account this introduces another parameter, in addition to that needed in Eq. (18) to describe the spin polarization of a degenerate 6*s* band.

C. Spin-orbit coupled bands

Finally, if the spin-orbit coupling of the conduction electrons is sufficient to split them into separate bands which we nominally label by their values $j = l \pm \frac{1}{2}$ we find for *d* electrons that three susceptibilities are needed. The expectation values for conduction-electron operators Eq. (19b) is now written

$$\langle B_z \rangle_d = - \sum_{\substack{jm_j \\ j'm_{j'}}} \langle jm_j | B_z | j'm_{j'} \rangle \langle j'm_{j'} | \mathcal{H}_{(4f)5d} | jm_j \rangle S(jj') , \tag{32}$$

where $S_{3/2\,3/2}$, $S_{3/2\,5/2}$, and $S_{5/2\,5/2}$ are the three different susceptibilies. When we place the 4*f*-5*d* exchange interaction Eq. (20) in this expression we find,

$$\langle l_z \rangle_d = \frac{\sqrt{10}}{6} a_1 c_1 \langle Y_{10}(\vec{L}) \rangle \sum_{jj'} (-)^{j+j'+1} \langle j || Y_1(\vec{l}) || j' \rangle \langle j' || Y_1(\vec{l}) || j \rangle S(jj')$$

$$+ \frac{2\sqrt{2}}{3} a_0 b_0 \langle Y_0(\vec{L}) S_z \rangle \sum_{jj'} (-)^{j+j'+1} \langle j || Y_1(\vec{l}) || j' \rangle \langle j' || \vec{s} || j \rangle S(jj')$$

$$+ \frac{2\sqrt{10}}{3} a_2 b_2 \langle [Y_2(\vec{L}) \times \vec{S}]^1_0 \rangle \sum_{jj'} (-)^{j+j'+1} \langle j || Y_1(\vec{l}) || j' \rangle \langle j' || [Y_2(\vec{l}) \times \vec{s}]^1 || j \rangle S(jj')$$

$$= \tfrac{1}{5} \sqrt{2/5}\, a_1 c_1 d_1 \langle Y_{10}(\vec{J}) \rangle (9S_{3/2\,3/2} + 2S_{3/2\,5/2} + 14S_{5/2\,5/2})$$

$$- \frac{4}{5\sqrt{5}} a_0 b_0 N^1_{01} \langle Y_{10}(\vec{J}) \rangle (3S_{3/2\,3/2} + 4S_{3/2\,5/2} - 7S_{5/2\,5/2})$$

$$+ \tfrac{4}{5} \sqrt{7/5}\, a_2 b_2 N^1_{21} \langle Y_{10}(\vec{J}) \rangle (3S_{3/2\,3/2} - S_{3/2\,5/2} - 2S_{5/2\,5/2}) , \tag{33}$$

$$
\begin{aligned}
\langle s_z\rangle_d &= \tfrac{1}{6}a_1c_1\langle Y_{10}(\vec{L})\rangle \sum_{jj'}(-)^{j+j'+1}\langle j\|\vec{s}\|j'\rangle\langle j'\|Y_1(\vec{l})\|j\rangle S(jj') \\
&\quad+\frac{2}{3\sqrt{5}}a_0b_0\langle Y_0(\vec{L})S_z\rangle \sum_{jj'}(-)^{j+j'+1}\langle j\|\vec{s}\|j'\rangle\langle j'\|\vec{s}\|j\rangle S(jj') \\
&\quad+\tfrac{2}{3}a_2b_2\langle [Y_2(\vec{L})\times\vec{S}]^1_0\rangle \sum_{jj'}(-)^{j+j'+1}\langle j\|\vec{s}\|j'\rangle\langle j'\|[Y_2(\vec{l})\times\vec{s}]^1\|j\rangle S(jj') \\
&= -\frac{1}{5\sqrt{10}}a_1c_1d_1\langle Y_{10}(\vec{J})\rangle(3S_{3/2\,3/2}+4S_{3/2\,5/2}-7S_{5/2\,5/2}) \\
&\quad+\frac{1}{5\sqrt{5}}a_0b_0N^1_{01}\,\langle Y_{10}(\vec{J})\rangle(2S_{3/2\,3/2}+16S_{3/2\,5/2}+7S_{5/2\,5/2}) \\
&\quad-\tfrac{2}{5}\sqrt{7/5}\,a_2b_2N^1_{21}\,\langle Y_{10}(\vec{J})\rangle(S_{3/2\,3/2}-2S_{3/2\,5/2}+S_{5/2\,5/2}) \ , \qquad (34)
\end{aligned}
$$

and

$$
\begin{aligned}
\langle [Y_2(\vec{l})\times\vec{s}]^1_0\rangle_d &= \tfrac{1}{6}a_1c_1\langle Y_{10}(\vec{L})\rangle \sum_{jj'}(-)^{j+j'+1}\langle j\|[Y_2(\vec{l})\times\vec{s}]^1\|j'\rangle\langle j'\|Y_1(\vec{l})\|j\rangle S(jj') \\
&\quad+\frac{2}{3\sqrt{5}}a_0b_0\langle Y_0(\vec{L})S_z\rangle \sum_{jj'}(-)^{j+j'+1}\langle j\|[Y_2(\vec{l})\times\vec{s}]^1\|j'\rangle\langle j'\|\vec{s}\|j\rangle S(jj') \\
&\quad+\tfrac{2}{3}a_2b_2\langle [Y_2(\vec{L})\times\vec{S}]^1_0\rangle \sum_{jj'}(-)^{j+j'+1}\langle j\|[Y_2(\vec{l})\times\vec{s}]^1\|j'\rangle\langle j'\|[Y_2(\vec{l})\times\vec{s}]^1\|j\rangle S(jj') \\
&= \tfrac{1}{25}\sqrt{7/2}\,a_1c_1d_1\langle Y_{10}(\vec{J})\rangle(3S_{3/2\,3/2}-S_{3/2\,5/2}-2S_{5/2\,5/2}) \\
&\quad-\tfrac{2}{25}\sqrt{7}\,a_0b_0N^1_{01}\,\langle Y_{10}(\vec{J})\rangle(S_{3/2\,3/2}-2S_{3/2\,5/2}+S_{5/2\,5/2}) \\
&\quad+\tfrac{1}{25}a_2b_2N^1_{21}\,\langle Y_{10}(\vec{J})\rangle(14S_{3/2\,3/2}+7S_{3/2\,5/2}+4S_{5/2\,5/2}) \ . \qquad (35)
\end{aligned}
$$

We note that all three expectation values depend only on $\langle J_z\rangle_{4f}$ independent of their origin, i.e., $\langle L_z\rangle$, $\langle S_z\rangle$, or $\langle Y_2(\vec{L})\times\vec{S}]^1_0\rangle$. In this model spherical symmetry is preserved and for this reason the expectation values of all time-odd vectorial quantities depend only on $\langle J_z\rangle$. When one makes the assumption that the three susceptibilities $S(jj')$ are equal we find Eqs. (33)–(35) once more reduce to Eqs. (26).

IV. DISCUSSION

In Secs. II–III we outlined the theoretical analysis of the contributions of conduction electrons to the magnetization and the hyperfine field at the rare-earth nucleus in cubic compounds. Our principal aim is to underline the existence of orbital contributions from conduction electrons to M_{cond} and H_{sp}. On symmetry arguments alone eight parameters $\xi(kpr)$ Eq. (4) are needed to describe the hyperfine field and another eight $\xi^m(kpr)$ Eq. (15a) are needed for the magnetization. There are not enough experimental data to determine the 16 parameters nor can we anticipate this in the future. It is necessary to reduce their number and in Sec. III we have shown how this can be done when we make assumptions about the conduction electrons.

When we place the expectation values $\langle l_z\rangle_d$, $\langle s_z\rangle_d$, and $\langle [Y_2(\vec{l})\times\vec{s}]^1\rangle_d$ derived from our model calculations, i.e., Eqs. (22)–(35), in Eq. (16) for the self-polarization field H_{sp} and Eq. (17) for the conduction-electron contribution to the magnetization M_{cond} we have a considerable reduction in the number of unknown parameters. In the expectation values Eqs. (22)–(35) the isotropic exchange constant a_0 can be put into the susceptibilities $S(n_1n_2)$ and the ratios of the exchange constants a_μ to a_0 are known from the atomic Slater integrals. The coupling coefficients b_μ, c_μ, d_μ, and $N^r_{\mu 1}$ are given in Tables I, IV, and V, and the expectation values of the $4f$ electron operators must be evaluated in the crystal- and molecular-field states of the rare-earth ions. In this manner we see that for M_{cond} we have three unknown parameters $a_0 S_{\alpha\beta}$ for the $5d$ electrons and one $a_0' \chi_s$ for the $6s$ electrons,[12] or a total of four unknown parameters. These *same* unknown parameters appear in the expression for the self-polarization field when we insert the expectation values $\langle l_z \rangle_d$, $\langle s_z \rangle_d$, and $\langle [Y_2(\vec{l}) \times \vec{s}]_0^1 \rangle_d$ in terms of the $a_0 S_{\alpha\beta}$ and $a_0' \chi_s$ in Eq. (16). To determine the self-polarization field three additional unknown parameters are needed, i.e., the coefficients A, B, and C entering Eq. (16).[13] In total *only seven parameters* are needed to fit both M_{cond} and H_{sp} if we resort to one of the specific models in Sec. III. This is a considerable reduction from the 16 parameters ξ needed in general.

The validity of the expressions derived in Sec. III can be tested by attempting to fit the data on H_{sp} and M_{cond}, see Refs. 1–5, to the seven unknown parameters. In the next article we evaluate the expressions for H_{sp} and M_{cond} based on Eqs. (22)–(35) and compare them to the extant experimental data on the rare-earth dialuminides (R = Nd, Sm, Gd, Tb, Dy, Ho, Er).

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[12] For a spin split $6s$ band an additional susceptibility $(S'_{++} - S'_{--})$ enters, but it is small compared to the other one $(S'_{++} + S'_{--})$.

[13] If one first fits H_{sp} five parameters are needed, and an additional two are needed to fit M_{cond}.