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Anisotropic exchange for dilute rare-earth alloys

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The exchange coupling between the $4f$ magnetic electrons and the $5d$-like screening electrons is calculated for Dy, Er, and Yb dilute magnetic alloys. The coupling is shown to be anisotropic, with significant orbital contributions for Dy and Yb. The g-shift expression is derived for arbitrary crystal-field splitting of the $5d$ virtual bound states. The linewidths are computed in the limit of no crystal-field splittings. Comparison with experiments on Dy and Er in Ag and Al hosts reveals good agreement.

I. INTRODUCTION

The magnetic resonance spectrum of dilute magnetic alloys has most often been interpreted using an isotropic exchange Hamiltonian $\mathcal{J}\vec{S}\cdot\vec{\sigma}$ between the magnetic ion and the conduction electrons. Strictly speaking, such an expression is only valid if the magnetic ion and the conduction electrons have no orbital angular momentum. The general form of the exchange coupling in the presence of orbital moment has been given by Liu,[1] Watson and Freeman,[2] Kaplan and Lyons,[3] and Levy.[4] Recently, Yang *et al.*[5] introduced orbital anisotropy in the exchange to fit the observed angular dependence of the ESR resonance field of Pd:Dy.[6]

We determine in this paper the strength of all the terms in the orbitally anisotropic exchange Hamiltonian from first principles. We then calculate the g shift and linewidth expected for rare-earth impurities in nonmagnetic hosts. This procedure is possible because the principal contribution to exchange for dilute rare-earth alloys arises from the interaction between the $4f$ and the $5d$-like screening conduction electrons.[7] The latter can be described by a virtual bound state (vbs) which, by virtue of its large width, is nonmagnetic in the metal. The interaction between the $4f$ and $5d$-like vbs is closely analogous to that of nuclei of nonmagnetic vbs's treated by Dworin and Narath.[8] Assigning $5d$ character to the vbs, all the exchange parameters can be related to the known Slater-Condon parameters. This is described in Sec. II A. We calculate the thermal average of the exchange in the presence of an applied magnetic field for a cubic crystal, using linear response theory, in Sec. II B.

We find that the orbital polarization of the vbs by the magnetic field contributes two terms to the exchange,

$$\chi_{\mathrm{orb}}\vec{L}\cdot\vec{H}$$

and

$$[Y_{3,0}(\vec{L})H_z - (\sqrt{3}/4)H_{3,-1}(\vec{L})H^+ - (\sqrt{5}/4)Y_{3,3}(\vec{L})H^+ + \mathrm{c.c.}],$$

whereas the spin polarization gives rise to

$$\chi_d\vec{S}\cdot\vec{H}$$

and

$$[\sqrt{\tfrac{7}{10}}\,Y_{4,0}(\vec{L}) + \tfrac{1}{2}Y_{4,4}(\vec{L}) + \tfrac{1}{2}Y_{4,-4}(\vec{L})]\vec{S}\cdot\vec{H}.$$

Here, χ_{orb} is the orbital susceptibility of the vbs. If we ignore the crystal-field splitting of the vbs, only the $\vec{L}\cdot\vec{H}$ and $\vec{S}\cdot\vec{H}$ terms survive (as expected). Because both $\vec{L}$ and $\vec{S}$ project into $\vec{J}$, the observed exchange coupling has contributions from both orbital and spin components. This will cause a difference in the effective exchange coupling as seen by ESR reflection measurements, and transmission-electron-spin-resonance (TESR) conduction-electron g-shift and linewidth measurements.

We use these expressions in Sec. III to calculate the g shift and linewidth for the Γ_7 doublet of Dy, Er, and Yb in cubic hosts. Numerical estimates for both quantities are given for two extreme cases: crystal-field splittings small and large compared to the screening $5d$ vbs level width. We find that the orbitally anisotropic term $Y_{4,\nu}(\vec{L})\vec{S}\cdot\vec{H}$ is important for Dy and Yb for large $5d$ vbs crystal-field splitting, but not for Er, for which a numerical cancellation occurs. The values of the linewidth are consistent with experiment, and in agreement with respect to absolute magnitude for reasonable values of the vbs level width.

II. THEORY

A. Orbitally anisotropic localized-conduction-electron exchange

The principal part of the exchange contribution to the ESR spectrum of the rare earth in dilute rare-earth alloys originates at the rare-earth site. The conduction electrons possess a $5d$-like character because of the orthogonality requirement to the occupied d orbitals,[9] and the necessity of screening the 3+ rare-earth core. The exchange interaction between a single $4f$ electron and a $5d$ electron can be written as[10]

$$H=-\sum_{\mu\nu\mu'\nu'} a_{\mu\nu\mu'\nu'}Y^*_{\mu\nu}(\vec{l}_i)Y_{\mu'\nu'}(\vec{l})(2\vec{s}_i\cdot\vec{s}+\tfrac{1}{2}), \qquad (1)$$

where $\vec{l}_i, \vec{s}_i$ and $(\vec{l}, \vec{s})$ refer, respectively, to the f electron and the $5d$ vbs electron. The spherical-harmonics are orthonormalized:

$$\sum_{m=-l}^{l}\langle m|Y^*_{\mu_1\nu_1}(\vec{l})Y_{\mu_2\nu_2}(\vec{l})|m\rangle=\delta_{\mu_1\mu_2}\delta_{\nu_1\nu_2}\,.$$

Van Vleck and Huang[10] showed that the coefficient $a_{\mu\nu\mu'\nu'}$ is related to the exchange integral $J(m_imm_i'm')$ as follows:

$$J(m_imm_i'm')=\langle m_im|\sum_{\mu\nu\mu'\nu'}a_{\mu\nu\mu'\nu'}\times Y^*_{\mu\nu}(\vec{l}_i)Y_{\mu'\nu'}(\vec{l})|m_i'm'\rangle, \qquad (2)$$

where

$$J(m_imm_i'm')=\int\psi^*_{m_i}(\vec{r}_1)\phi^*_m(\vec{r}_2)\frac{e^2}{r_{12}}\psi_{m_i'}(\vec{r}_2)\times\phi_{m'}(\vec{r}_1)\,d\vec{r}_1d\vec{r}_2, \qquad (3)$$

with ψ and ϕ referring, respectively, to the $4f$ and $5d$ orbitals. To express the $a_{\mu\nu\mu'\nu'}$ in terms of J, we multiply (2) by $\langle m_i'|Y_{\mu\nu}(\vec{l}_i)|m_i\rangle\times\langle m'|Y_{\mu'\nu'}(\vec{l})|m\rangle$ and sum over m_i, m_i', m, and m'. We find

$$a_{\mu\nu\mu'\nu'}=\sum_{m_im_i'mm'}\langle m_i'|Y_{\mu\nu}(\vec{l}_i)|m_i\rangle\times\langle m'|Y^*_{\mu\nu}(\vec{l})|m\rangle J(m_imm_i'm'). \qquad (4)$$

The spherical symmetry exhibited in (3) further restricts $a_{\mu\nu\mu'\nu'}=0$ if $\mu\neq\mu'$ and $\nu\neq\nu'$. In addition, for a given μ, $a_{\mu\nu\mu\nu}$ is independent of ν. The exchange integrals J can be expressed in terms of the Slater-Condon integrals G_i following Condon and Shortley.[11] Calling $a_{\mu\nu\mu\nu}\equiv a_\mu$, we find

$$\begin{aligned}
a_0&=(3G_1+\tfrac{4}{3}G_3+\tfrac{50}{33}G_5)/\sqrt{35}\,,\\
a_1&=(4G_1+\tfrac{2}{3}G_3-\tfrac{50}{33}G_5)/\sqrt{70}\,,\\
a_2&=(\tfrac{36}{5}G_1-\tfrac{22}{15}G_3+\tfrac{50}{33}G_5)/7\sqrt{6}\,,\\
a_3&=(\tfrac{9}{7}G_1-\tfrac{8}{21}G_3-\tfrac{25}{231}G_5)/\sqrt{15}\,,\\
a_4&=(11G_1+\tfrac{44}{9}G_3+\tfrac{25}{99}G_5)/7\sqrt{55}\,.
\end{aligned} \qquad (5)$$

All the other a_μ with $\mu>4$ must vanish for the $4f$-$5d$ interaction by virtue of the triangle rule. Using the values for G_i calculated by Freeman and Mallow,[12] we list a_μ for Dy, Er, and Yb in Table I. Upon summing over the $4f$ electrons in (1), we obtain the following expression for the rare-earth–conduction-electron exchange:

$$H=-\sum_{\mu=0}^{4}\sum_{\nu=-\mu}^{\mu}a_\mu Y^*_{\mu\nu}(\vec{L})Y_{\mu\nu}(\vec{l})(2b_\mu\vec{S}\cdot\vec{s}+\tfrac{1}{2}c_\mu), \qquad (6)$$

where b_μ and c_μ are projection factors defined by

$$\sum_i Y_{\mu\nu}(\vec{l}_i)\vec{s}_i=b_\mu Y_{\mu\nu}(\vec{L})\vec{S} \qquad (7a)$$

and

$$\sum_i Y_{\mu\nu}(\vec{l}_i)=c_\mu Y_{\mu\nu}(\vec{L}). \qquad (7b)$$

The values for b_μ and c_μ are listed in Table II.

It should be pointed out that the exchange contribution to the cubic crystal field potential for the rare-earth ion can be obtained from (6) in a straightforward manner. To illustrate the procedure, we follow the assumption of Chow[13] that the conduction electrons occupy equally the three (nonmagnetic) $5d$-t_{2g} states. In the absence of a magnetic field, the expectation value of $Y_{\mu\nu}(\vec{l})\vec{s}$ is obviously zero, so that only the purely orbital part of (6) contributes. We find

$$\langle H\rangle=(a_4c_4/6)[\sqrt{\tfrac{7}{10}}Y_{4,0}(\vec{L})+\tfrac{1}{2}Y_{4,4}(\vec{L})+\tfrac{1}{2}Y_{4,-4}(\vec{L})].$$

This is simply the exchange correction of Chow[13] to the fourth-degree crystal-field potential for the

TABLE I. Exchange parameters (in cm^{-1}) as calculated from Eq. (5).

	Er	Dy	Yb
a_0	8862.3	8758.2	8577.1
a_1	4430.8	4363.0	4295.6
a_2	4185.6	4126.9	4055.5
a_3	2401.1	2361.3	2328.6
a_4	3029.6	2991.5	2934.2

TABLE II. Projection factors defined in Eqs. (7a) and (7b).

	c_0	c_1	c_2	c_3	c_4	b_0	b_1	b_2	b_3	b_4
Er	14.9905	2.5495	−0.4438	−0.8876	0.6371	1.3628	−0.8498	0.1479	0.2959	−0.2124
Dy	11.2821	1.9821	1.0653	0	−2.7255	1.2536	−0.3964	−0.2131	0	0.5451
Yb	13	1	−1	1	−1	1	−1	1	−1	1

rare-earth $4f$ electrons. Our numerical values for $\langle H\rangle$ agree well with those of Chow,[13] serving as a useful numerical check on our method. We emphasize that this term originates from the factor $\frac{1}{2}$ in (1), rather than the spin-dependent part. In the presence of an applied magnetic field, we shall see in Sec. II B that the purely orbital part of H will give rise to important contributions to the magnetic resonance g shift and linewidth as well.

B. Thermal average of the exchange interaction

For rare-earth ions in most metallic hosts, the screening electrons can be characterized as $5d$-like in the vicinity of the ion. This orbital is nonmagnetic because of its rather large "occupation" width, and can accurately be described as a virtual bound state.[14] The $5d$ orbitals will split in the presence of the crystalline-field environment (in the present case, cubic), and one of the critical parameters of our theory will be the ratio of this splitting to the vbs width Δ. Because this ratio can be large, we shall formulate the g-shift and linewidth expressions in terms of the properties of the vbs t_{2g} and e_g orbitals, allowing for different energies (i.e., for a vbs crystal-field splitting) and different widths (not unrelated to the vbs crystal-field splitting).

To calculate the thermal average of the exchange in an applied magnetic field, we follow the method used by Dworin and Narath.[8] To compute the g shift, we need only evaluate the static thermal average of the conduction-electron operators in (6). The Zeeman interaction between the conduction electrons and the applied magnetic field is given by $-\mu_B\vec{1}\cdot\vec{H}-2\mu_B\vec{s}\cdot\vec{H}$. It is easy to see that the orbital part of the Zeeman interaction contributes to $\langle Y_{\mu\nu}(\vec{1})\rangle$ in (6), whereas the spin part contributes to $Y_{\mu\nu}(\vec{1})\vec{s}$. We label the $5d$ states by

$$t_{2g}:\ \ \phi_1=|2,1\rangle,\quad \phi_2=(1/\sqrt{2})(|2,2\rangle-|2,-2\rangle),$$

$$\phi_3=|2,-1\rangle;$$

$$e_g:\ \ \phi_4=|2,0\rangle,\quad \phi_5=(1/\sqrt{2})(|2,2\rangle+|2,-2\rangle).$$

We find, in a manner similar to the calculation of $\langle\vec{1}\rangle$ by Dworin and Narath,[8]

$$\langle Y_{\mu\nu}(\vec{1})\rangle=\sum_{i,j}\langle\phi_i|Y_{\mu\nu}(\vec{1})|\phi_j\rangle \times\langle\phi_j|2\vec{1}\cdot\vec{H}|\phi_i\rangle\tilde{S}(\phi_j,\phi_i,0)\mu_B, \tag{8}$$

where $\tilde{S}(\phi_j,\phi_i,0)$ is the effective static orbital density matrix defined by[8]

$$\tilde{S}(\phi_j,\phi_i,0)=\chi^0(\phi_j,\phi_i,0)[1-(U-J)\tilde{S}(\phi_j,\phi_i,0)], \tag{9}$$

with $\chi^0(\phi_j,\phi_i,0)$, the generalized unenhanced susceptibility, given by

$$\chi^0(\phi_j,\phi_i,0)=\frac{\hbar}{2\pi i}\int d\omega f(\omega)[G^{>}(\phi_j,\omega)G^{>}(\phi_i,\omega)-G^{<}(\phi_j,\omega)G^{<}(\phi_i,\omega)],$$

where $f(\omega)$ is the Fermi function, and $G^{\gtrless}(\phi_i,\omega)$ the Green's functions given by $G^{\gtrless}(\phi_i,\omega)=[\hbar\omega-E(\phi_i)\pm i\Delta(\phi_i)]^{-1}$. In the limit $kT\ll\Delta$, we find (using the notation $t_{2g}=t$, $e_g=e$)

$$\chi^0(t,t,0)=\Delta_t(\Delta_t^2+E_t^2)/\pi,$$

$$\chi^0(e,e,0)=\Delta_e(\Delta_e^2+E_e^2)/\pi,$$

$$\chi^0(t,e,0)=\chi^0(e,t,0)=\frac{(E_t-E_e)(\theta_t-\theta_e)-(\Delta_t-\Delta_e)(\ln r_t-\ln r_e)}{\pi[(\Delta_t-\Delta_e)^2+(E_t-E_e)^2]},$$

where $\theta_t=\tan^{-1}(\Delta_t/E_t)$, $r_t=(\Delta_t^2+E_t^2)^{1/2}$, with similar expressions for the e states. We note that $\chi^0(t,e,0)$ reduces to $\chi^0(t,t,0)$ in the limit $\Delta_t=\Delta_e$ and $E_t=E_e$. Evaluating the matrix elements in (8), we find the following expression for the thermal average of the orbital part of the exchange:

$$-\frac{1}{2}\sum_{\mu,\nu}a_\mu c_\mu Y^*_{\mu,\nu}(\vec{L})\langle Y_{\mu,\nu}(\vec{1})\rangle=\frac{a_1c_1}{2\sqrt{10}|\mu_B|}\chi_{\text{orb}}(0)\left\{Y_{1,0}(\vec{L})H_z+\frac{1}{\sqrt{2}}Y_{1,-1}(\vec{L})H^+-\tfrac{1}{2}Y_{1,1}(\vec{L})H^-\right\}$$
$$+\frac{a_3c_3}{\sqrt{10}|\mu_B|}[\chi_{\text{orb}}(t,e,0)-\chi_{\text{orb}}(t,t,0)]$$
$$\times\{Y_{3,0}(\vec{L})H_z-\tfrac{1}{4}[\sqrt{3}Y_{3,-1}(\vec{L})+\sqrt{5}Y_{3,3}(\vec{L})]H^++\tfrac{1}{4}[\sqrt{3}Y_{3,1}(\vec{L})+\sqrt{5}Y_{3,-3}(\vec{L})]H^-\}, \tag{10}$$

where the static orbital susceptibility is defined by

$$\chi_{\text{orb}}(0)=\chi_{\text{orb}}(t,t,0)+4\chi_{\text{orb}}(t,e,0),$$

with

$$\chi_{\text{orb}}(t,t,0)=4\mu_B^2\tilde{S}(t,t,0),$$

$$\chi_{\text{orb}}(t,e,0)=4\mu_B^2\tilde{S}(t,e,0).$$

The products of the spherical harmonics and the magnetic field in each pair of curly brackets in (10) transform as the identity representation of the cubic group. No even degree spherical harmonics appears in (10) because of time-reversal symmetry.

The spin contribution to the g shift will also involve orbital terms. We must calculate the average of $Y_{\mu\nu}(\vec{l})Y^*_{\mu\nu}(\vec{L})\vec{S}\cdot\vec{s}$. Because of time-reversal symmetry, the average will vanish for μ an odd integer. Initially, we simplify the computation by considering $\nu=0$ only. We shall add the $\nu\neq 0$ terms by constructing the cubic invariant later. We find

$$\langle Y_{\mu,0}(\vec{l})\vec{\sigma}_z\rangle=\sum_{i,j}\langle\phi_i|Y_{\mu,0}(l)|\phi_i\rangle\times S(\phi_i,\phi_j,0)\mu_B H_z,\quad \mu=0,2,4. \tag{11}$$

Only the diagonal matrix elements of $Y_{\mu,0}$ exist for μ equal to an even integer. The effective-spin-density matrix $S(\phi_i,\phi_j,0)$ obeys the Bethe-Salpeter equation[8]

$$S(\phi_i,\phi_j,0)=\chi(\phi_i,\phi_i,0)\Big(\delta_{ij}+US(\phi_i,\phi_j,0)+J\sum_k S(\phi_k,\phi_j,0)\Big). \tag{12}$$

From (11) and (12), we obtain the following average for the spin part of the exchange:

$$-2\sum_{\mu,\nu}a_\mu b_\mu Y^*_{\mu\nu}(\vec{L})\vec{S}\cdot\langle\vec{s}Y_{\mu\nu}(\vec{l})\rangle=\frac{a_0b_0\chi_d(0)}{[5(2L+1)]^{1/2}|\mu_B|}\vec{S}\cdot\vec{H}+2a_4b_4|\mu_B|\left(1+\frac{J\chi_d(0)}{2\mu_B^2}\right)\left(\frac{\chi^0(e,e,0)}{1-U\chi^0(e,e,0)}-\frac{\chi^0(t,t,0)}{1-U\chi^0(t,t,0)}\right)$$

$$\times\vec{S}\cdot\vec{H}[\sqrt{\tfrac{7}{10}}Y_{4,0}(\vec{L})+\tfrac{1}{2}Y_{4,4}(\vec{L})+\tfrac{1}{2}Y_{4,-4}(\vec{L})], \tag{13}$$

where the static spin susceptibility $\chi_d(0)$ is given by[8]

$$\chi_d(0)=2\mu_B^2\sum_{i,j}S(\phi_i,\phi_j,0),$$

with

$$\sum_{i,j}S(\phi_i,\phi_j,0)=\left(\frac{3\chi^0(t,t,0)}{1-U\chi^0(t,t,0)}+\frac{2\chi^0(e,e,0)}{1-U\chi^0(e,e,0)}\right)\left(1-\frac{3J\chi^0(t,t,0)}{1-U\chi^0(t,t,0)}-\frac{2J\chi^0(e,e,0)}{1-U\chi^0(e,e,0)}\right)^{-1}.$$

In the absence of crystal-field splitting of the $5d$ electron orbitals ($E_t=E_e$), only $\vec{S}\cdot\vec{s}$ and $Y^*_{1,\nu}(\vec{L})\times Y_{1,\nu}(\vec{l})$ terms survive. This follows from the fact that only the $\mu=1$ term in (8) and the $\mu=0$ term in (11) contribute as a consequence of the orthogonality relation. Indeed, (10) and (13) reduce to, respectively, the terms $\chi_{\text{orb}}(0)\vec{L}\cdot\vec{H}$ and $\chi_d(0)\vec{S}\cdot\vec{H}$ in the absence of a crystalline field.

The energies E_t and E_e of the $5d$ vbs electrons are related to one another through the condition that the number of $5d$ screening electrons is determined by the Friedel sum rule. Usually, one expects only a single screening electron of $5d$ character as a consequence of charge neutrality (with two others in $6s$-like orbits). From the expression for the $5d$ vbs density of states, this leads to

$$(2/\pi)[2\cot^{-1}(E_e/\Delta_e)+3\cot^{-1}(E_t/\Delta_t)]=1. \tag{14}$$

To calculate the exchange contribution to the g shift of the rare-earth ions, we need to project $Y_{\mu\nu}(\vec{L})$ and $Y_{\mu\nu}(\vec{L})\vec{S}$ onto the effective-spin operator $\tilde{S}$. This is done for the Γ_7 ground doublet of Dy, Er, and Yb by defining

$$Y_{\mu,0}(\vec{L})=d_\mu Y_{\mu,0}(\vec{J})=d_\mu e_{\mu,0}\tilde{S}_z, \tag{15a}$$

$$Y_{0,0}(\vec{L})S_z=N_1Y_{1,0}(\vec{J})=N_1e_{1,0}\tilde{S}_z, \tag{15b}$$

$$Y_{4,0}(\vec{L})S_z=-\tfrac{2}{3}N_3Y_{3,0}(J)+(\sqrt{5}/3)N_5Y_{5,0}(\vec{J})=-\tfrac{2}{3}N_3e_{3,0}\tilde{S}_z+(\sqrt{5}/3)N_5e_{5,0}\tilde{S}_z, \tag{15c}$$

$$Y_{4,\pm 4}(\vec{L})S_z=(1/\sqrt{5})N_5e_{5,\pm 4}\tilde{S}_z. \tag{15d}$$

The appropriate values for d_μ, N_μ, and $e_{\mu,\nu}$ are listed in Table III. A quantitative result for the g shift Δg and thermal linewidth $1/T_2$ requires the knowledge of Δ_t,Δ_e, E_t, E_e, U, and J. Such detailed information is not yet available for the $5d$ vbs for rare earths, though optical experiments can yield rough estimates. We shall evaluate both Δg and $1/T_2$ in Sec. III in the limit of small crystal-field splitting; and the g shift in the limit of large

TABLE III. Projection factors defined by Eqs. (15a) and (15b).

	d_1	d_3	N_1	N_3	N_5	$e_{1,0}$	$e_{3,0}$	$e_{5,0}$	$e_{5,\pm4}$
Er	1.0934	1.0147	1.0228	−0.8372	1.3319	0.3072	0.0860	−0.3214	0.1211
Dy	1.1721	1.0101	1.8532	7.1754	2.0755	0.3072	0.0860	−0.3214	0.1211
Yb	1.0498	0.9476	0.3499	−0.1870	0.6015	0.4629	−0.2462	−0.9201	−0.2685

crystal-field splitting. The results will be instructive, indicating the trend of the orbital exchange strength as a function of $(E_t-E_e)/\Delta$.

III. g SHIFT AND LINEWIDTH

We first consider the g shift Δg for the two extreme limits.

A. Small-crystal-field splitting [$|(E_t-E_e)/\Delta|<1$]

For this case, $\chi_{\text{orb}}(t,e,0)=\chi_{\text{orb}}(t,t,0)$ and $\chi^0(e,e,0)=\chi^0(t,t,0)$. Only the $\vec{L}\cdot\vec{H}$ term in (10) and the $\vec{S}\cdot\vec{H}$ term in (13) survive. The solution to (14) is given by $E_t=E_e=E=3.078\Delta$. Substituting this value for E, and (15), into (10) and (13), we obtain

$$\Delta g=0.137a_0b_0N_1e_{1,0}/\Delta+0.096a_1c_1d_1e_{1,0}/\Delta. \quad (16)$$

The first term originates with $\vec{L}\cdot\vec{l}$ and the second with $\vec{S}\cdot\vec{s}$ in (6). Numerical estimates for Δg are listed in Table IV. We see that the orbital contribution can be as large as the spin contribution to Δg. For rare earths in Al, it is expected that $\Delta\sim2.5$ eV. This value, and those of Table IV, yield

$$\Delta g(\text{Al}:\text{Dy})=0.06,\quad \Delta g(\text{Al}:\text{Er})=0.04.$$

These values are in good agreement with experiment.[15]

TABLE IV. Orbital and spin contributions to the g shift for a small-crystal-field splitting of the $5d$ vbs. The width Δ of the vbs is expressed in units of eV.

	Er	Dy	Yb
Δg(from $\vec{L}\cdot\vec{l}$)	$0.045/\Delta$	$0.037/\Delta$	$0.025/\Delta$
Δg(from $\vec{S}\cdot\vec{\sigma}$)	$0.064/\Delta$	$0.106/\Delta$	$0.024/\Delta$
Δg(total)	$0.109/\Delta$	$0.143/\Delta$	$0.049/\Delta$

B. Large-crystal-field splitting ($E_t\ll E_e$; $E_e-E_t\gg\Delta$)

From the condition (14), we find $E_t=\sqrt{3}\Delta_t$. In such a limit, all of the terms in (10) and (13) contribute to Δg. Expressing (10) and (13) in terms of fictitious spin, we obtain

$$\begin{aligned}\Delta g=\{&0.050a_1c_1d_1e_{1,0}-0.100a_3c_3d_3e_{3,0}\\&+0.213a_0b_0N_1e_{1,0}-0.089a_4b_4N_3e_{5,0}\\&-a_4b_4N_5[0.100e_{5,0}+0.036(e_{5,4}+e_{5,-4})]\}/\Delta.\end{aligned}$$

Here, the first term originates with $\vec{L}\cdot\vec{l}$, the second with $Y_{3,\nu}(\vec{L})Y_{3,\nu}(\vec{l})$, the third with $\vec{S}\cdot\vec{s}$, and the last four with $Y_{4,\nu}(\vec{L})Y_{4,\nu}(\vec{l})\vec{S}\cdot\vec{s}$ in (6). Numerical estimates for Δg are given in Table V. For Dy and Er, the major contributions arise from $\vec{S}\cdot\vec{s}$, though the contribution from $\vec{L}\cdot\vec{l}$ [and $Y_{4,\nu}(\vec{L})Y_{4,\nu}(\vec{l})\vec{S}\cdot\vec{s}$ for Dy] is also numerically important. For Yb, all three terms yield roughly the same contribution. In this case the exchange cannot be represented within the ground J multiplet by an effective $\vec{S}\cdot\vec{s}$ interaction because of the presence of the terms $Y_{3,\nu}(\vec{L})$ and $Y_{4,\nu}(\vec{L})\vec{S}$, (though, of course, it can be projected onto an effective-spin $\vec{\mathfrak{s}}$ space within, say, a ground doublet).

The linewidth is easily calculable in the small-crystal-field limit (it is far more complicated in the large-crystal-field limit, which does not warrant our attention at this time). Using the same approach as that of Dworin and Narath,[8] we find

$$\begin{aligned}1/T_2=&(\pi/5\hbar)e_{1,0}^2(4a_0^2b_0^2N_1^2+a_1^2c_1^2d_1^2)\\&\times N_d^2(E_F)k_BT.\end{aligned}\quad (17)$$

The first term arises from the spin-dependent part of (6), and the second from the orbital part. There is no cross term. Using the values exhibited in Tables I–III, (17) can be evaluated easily for, say, the Γ_7 ground state of Er. One finds an

TABLE V. Contributions to the g shift assuming the $5d$ e_g states to have energies much larger than the $5d$ $t_{2g}+\Delta$ energy. The width Δ_t of the t_{2g} states is expressed in eV.

	Er	Dy	Yb
Δg(from $\vec{L}\cdot\vec{l}$)	$0.024/\Delta_t$	$0.019/\Delta_t$	$0.013/\Delta_t$
Δg[from $Y_{3,\nu}^{*}(\vec{L})Y_{3,\nu}(\vec{l})$]	$0.002/\Delta_t$	0	$0.007/\Delta_t$
Δg(from $\vec{S}\cdot\vec{\sigma}$)	$0.100/\Delta_t$	$0.165/\Delta_t$	$0.037/\Delta_t$
Δg[from $Y_{4,\nu}^{*}(\vec{L})Y_{4,\nu}(\vec{l})\vec{S}\cdot\vec{\sigma}$]	$-0.002/\Delta_t$	$0.021/\Delta_t$	$0.026/\Delta_t$
Δg(total)	$0.124/\Delta_t$	$0.205/\Delta_t$	$0.083/\Delta_t$

equivalent linewidth:

$$\Delta H/\Delta T = 34.9/\Delta^2 \text{ G/K}, \tag{18}$$

where Δ is expressed in eV. For Al, where $\Delta \sim 2.5$ eV, this leads to $\Delta H/\Delta T = 4.8$ G/K, somewhat smaller than reported in Ref. 15. It is interesting to compute the ratio of $\Delta H/\Delta T$ for Dy and Er. This ratio should be independent of the value of Δ. Using Tables I–III, we find

$$(\Delta H/\Delta T)_{\text{Dy}}/(\Delta H/\Delta T)_{\text{Er}} = 2.30\,. \tag{19}$$

If one considers only isotropic exchange in (6), i.e., $-2a_0 b_0 Y_{00}(\vec{L}) Y_{00}(\vec{l}) \vec{S}\cdot\vec{s}$, this ratio will be given by $[a_0(g_J - 1)]^2_{\text{Dy}}/[a_0(g_J - 1)]^2_{\text{Er}} = 2.71$. Here, g_J is the Landé g factor, equal to $\frac{4}{3}$ for Dy, and $\frac{6}{5}$ for Er. Experimentally, this ratio varies between 2.6 for an Al host, to 2.3 for an Ag host.[16]

This trend is interesting, for it is in accordance with our ideas about vbs widths Δ in Al and Ag. They are expected to be much larger for d electrons in Al as compared to Ag. This will cause the linewidth contribution arising from screening electrons [$\Delta H/\Delta T$ varies as $1/\Delta^2$ according to (17)] to diminish substantially for Al as compared to Ag hosts. One therefore expects the major contribution to $\Delta H/\Delta T$ in Al to arise from the running-wave conduction electrons at the rare-earth site. These will be predominantly of s- and p-like character, and will therefore couple to the $4f$ electrons with primarily isotropic exchange.[17] The ratio of Dy-to-Er linewidths in Al would then equal 2.71. Experimentally,[15] it is found to equal 2.6 for the Al host. For the Ag host, the vbs width is significantly smaller than for Al, and one expects the screening d-like electron contribution to be relatively larger. For vbs width ≫ crystal-field splitting, the Dy-to-Er linewidth ratio would equal 2.30 [See Eq. (19)]. Experimentally[16] one finds 2.3.

Apparently the vbs dominates in the Ag host. Putting these results together, the s- and p-like contributions to $\Delta H/\Delta T$ are expected to be smaller than the vbs contributions for rare earths in Ag than in Al.

If one had complete confidence in (17), one could use the experimental linewidth ratio for Dy and Er to determine the contribution of the d-like vbs to the linewidth, separate from that of the s- and p-like conduction electrons. Our lack of precise knowledge of the radial part of the screening-electron wave function, and the approximate character of the Cohen-Heine cancellation theorem, combine to reduce the accuracy of such a computation. When more accurate vbs wave functions become available, it would be interesting to carry out such a separation. For the present, the trend is in accordance with our microscopic picture of rare earths dissolved in simple metal hosts.

IV. CONCLUSIONS

By treating the conduction electron, in the vicinity of the rare-earth ion, as an atomic $5d$-like screening electron, we are able to express the anisotropy in the exchange in terms of the spherical harmonics $Y^*_{\mu\nu}(\vec{L}) Y_{\mu\nu}(\vec{l})$. Coqblin and Schrieffer[18] derived an anisotropic exchange by making the Schrieffer-Wolff transformation for the localized-conduction-electron interaction in the Anderson Hamiltonian, taking into account combined spin and orbit exchange scattering. Within the approximation of taking the conduction electron as atomiclike, one can show that our exchange Hamiltonian (1) is identical to theirs.[19]

We have demonstrated here the importance of anisotropic exchange to the ESR spectrum in dilute rare-earth alloys. Orbital anisotropy will also affect the nuclear magnetic relaxation properties in magnetic alloys, and we will discuss this effect in a forthcoming paper.

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