Magnetotransport properties of noble metals containing rare-earth impurities.
II. Theory*

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Rare-earth impurities in noble metals induce an anisotropic magnetoresistance and a skew scattering contribution to the Hall resistivity. These effects are due to anisotropic terms of the $4f$–conduction-electron interaction, but an estimate of these terms based on conduction electrons in plane-wave states gives values too small to explain the experimental data. We have taken into account the admixture of $5d$ screening electrons into the conduction band, and we obtain a $4f$–conduction-electron interaction which has large anisotropic terms in addition to the conventional spin interaction. We have used in this calculation atomic $4f$-$5d$ Slater integrals, and we also had to estimate the width of the $5d$ virtual bound state. When we assume that the $5d$ electrons are in t_{2g} states, we find that our estimate of the anisotropy of the magnetoresistance and of the skew scattering effect are in fair agreement with the experimental data. However, we find too large a negative isotropic magnetoresistance.

I. INTRODUCTION

Rare-earth impurities in noble metals give rise to an anisotropic magnetoresistance and to an extraordinary Hall effect. It has previously been shown by Friederich and Fert[1-4] that these result from the anisotropy of the $4f$-conduction-electron interaction. In this paper we present a calculation of the anisotropic terms of this interaction and we determine their contribution to magnetoresistance and to the Hall effect. Our basic idea is to explain the observed anisotropy by the $5d$ electrons (localized on the rare earth) which are admixed with the conduction electrons of the noble metal, i.e., by the formation of a nonmagnetic $5d$ virtual bound state (VBS). The conduction electrons can strongly feel the orbital anisotropy of the $4f$ shell because the admixed $5d$ states lie close to the $4f$ electrons.

The formation of a nonmagnetic VBS on a trivalent rare-earth (RE) ion in a monovalent noble metal has been demonstrated by several experiments[5-7] and has been used in several model calculations. Williams and Hirst[8] and Chow[9] were able to account for the crystal field acting on the $4f$ electrons (of the RE impurity) by considering the contribution of their Coulomb interaction with the $5d$ electrons of the VBS and by using the $4f$-$5d$ Coulomb integrals obtained from atomic Hartree-Fock calculations. Recently Huang Liu et al.[10] interpreted the EPR g shift and linewidth of RE impurities in silver and aluminum by taking into account the exchange part of the same $4f$-$5d$ interaction. Our problem is somewhat different from those treated by Williams and Hirst, Chow, or Huang Liu et al. in that we are not directly interested in the $4f$-$5d$ interaction

at a RE site but we do use this interaction to determine its contribution to the anisotropic scattering of conduction electrons; i.e., we express the $4f$–conduction-electron interaction in terms of the $4f$-$5d$ interaction.

We begin by briefly describing the several magnetotransport effects which depend on the magnetization of RE impurities in noble metals.

A. Anisotropic magnetoresistance

For gold or silver containing RE impurities with an orbital moment, the dominant contribution to the magnetoresistance is anisotropic.[1,2,4] In polycrystalline samples it varies as $\cos^2\theta - \frac{1}{3}$, where θ is the angle between the field and the current. This anisotropic magnetoresistance is mostly induced by the quadrupolar terms of the Coulomb interaction between $4f$ and conduction electrons. When the interaction is limited to the partial wave with $l = 2$, the relevant quadrupolar term can be written, in the notation of Fert et al.,[4] as

$$V_{qd} = -4\pi \frac{D^{(2)}}{N} \left(J_z^2 - \frac{J(J+1)}{3} \right)$$
$$\times \sum_{\vec{k},\vec{k}',m} \left(1 - \frac{m^2}{2} \right) Y_{2m}^*(\Omega_{\vec{k}}) Y_{2m}(\Omega_{\vec{k}'}) a_{\vec{k}}^\dagger a_{\vec{k}'},$$

(1)

where N is the number of atoms per unit volume.

B. Negative isotropic magnetoresistance

This second contribution to the magnetoresistance does not depend on the angle between the field and the current. It is a well-known effect which is due

to the usual isotropic exchange interaction between the spins of conduction and localized electrons. When the interaction is limited to partial waves with $l = 2$ of the conduction electrons, the isotropic exchange interaction between conduction and $4f$ spins can be written, in the notation of Fert et al.,[4] as

$$V_{\text{exch}} = -2\pi(g_J - 1)\frac{\Gamma^{(2)}}{N}\sum_{\vec{k},\vec{k}',m} Y_{2m}^*(\Omega\,\vec{k})Y_{2m}(\Omega\,\vec{k}')$$

$$\times[(a_{\vec{k}'+}^\dagger a_{\vec{k}+} - a_{\vec{k}'-}^\dagger a_{\vec{k}-})J_z$$

$$+ a_{\vec{k}'+}^\dagger a_{\vec{k}-}J^- + a_{\vec{k}'-}^\dagger a_{\vec{k}+}J^+]. \qquad (2)$$

C. Contribution of skew scattering to the Hall effect

This contribution to the Hall effect, which is proportional to the magnetization of the impurities, is induced by terms of the scattering potential which depend on the orbital angular momentum $\vec{l}$ of the conduction electrons. For rare-earth impurities in noble metals,[2,3] the skew scattering is due to both the spin-orbit coupling of the conduction electrons and terms like $\vec{l} \cdot \vec{L}$ in the exchange interaction between the conduction and $4f$ electrons. In this paper we do not discuss the spin-orbit coupling contribution. The only term of $\vec{l} \cdot \vec{L}$ which contributes to skew scattering is $l_z L_z$.[3] This can be written as

$$V_{\text{skew}} = -4\pi\frac{\Lambda^{(2)}}{N}(2 - g_J)J_z$$

$$\times \sum_{\vec{k},\vec{k}',m} m\, Y_{2m}^*(\Omega\,\vec{k})Y_{2m}(\Omega\,\vec{k}')a_{\vec{k}'}^\dagger a_{\vec{k}}. \qquad (3)$$

Up to now, experiments on gold and silver containing rare-earth impurities have not been interpreted[3] with Eq. (3) but with an interaction of the same type acting on the $l = 1$ partial waves. We will show that the $l = 2$ term is much larger.

From Eqs. (1)–(3) we can see that the magnetotransport properties probe different aspects of the $4f$-conduction-electron interaction; i.e., the quadrupolar term, the spin exchange term $\vec{s} \cdot \vec{S}$, and the orbital exchange term $\vec{l} \cdot \vec{L}$ contribute to different properties. The EPR g shift and linewidth of rare-earth impurities in noble metals also have contributions from the spin and orbital exchange terms.[10] Nonetheless, the advantage of the magnetotransport experiments is that they single out different terms in the $4f$-conduction-electron interaction.

The magnitude of the coefficients $D^{(2)}$ and $\Lambda^{(2)}$ calculated on the basis of conduction electrons in plane-wave states are much smaller than the measured values. For this reason we have calculated these terms on the basis of a model which has a

$5d$ VBS. To obtain the magnitudes of the $4f$-conduction-electron scattering matrix elements, we used the atomic $4f$-$5d$ Coulomb and exchange integrals determined from the Hartree-Fock calculation by Freeman and Mallow.[11] The half width of the $5d$ VBS which enters these matrix elements is not well known, but for a reasonable value of this parameter we obtain a value of the anisotropy in good agreement with the experimental value. We are unable to obtain a definitive estimate of the skew scattering contribution to the Hall effect from the model calculation, because the p-wave screening Z_1 is poorly known. When we used the value $Z_1 = 0.1$, we found the skew scattering contribution was larger than that extrapolated from experimental data. In both calculations we found that the numerical estimates improved considerably when we considered the $5d$ electron in a cubic-crystal-field VBS rather than unsplit. This result is in agreement with the calculations of Williams and Hirst[8] and of Chow.[9]

II. CALCULATION

We begin by writing down the $4f$-$5d$ Coulomb interaction. Then we use this interaction to determine the $4f$-conduction-electron interaction.

A. 4f-5d Coulomb interaction

The Coulomb interaction between $4f$ and $5d$ atomic electrons on the same center can be written as[12]

$$H = \sum_k \left(F^k(4f, 5d)(3\|C^{(k)}\|3)(2\|C^{(k)}\|2) \right.$$

$$+ \sum_r (-)^{r+k}(2k+1)G^r(4f, 5d)(2\|C^{(r)}\|3)^2$$

$$\left. \times \begin{Bmatrix} 3 & 3 & k \\ 2 & 2 & r \end{Bmatrix}(\tfrac{1}{2} + 2\vec{s}_a \cdot \vec{s}_b) \right) u_a^{(k)} \cdot u_b^{(k)}, \qquad (4)$$

where F^k and G^r are the direct and exchange Slater integrals. The reduced matrix elements of the spherical harmonics are

$$(l\|C^{(k)}\|l') = (-)^l[(2l+1)(2l'+1)]^{1/2}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}, \qquad (5)$$

where the expression in large parentheses is a 3-j symbol. The symbol in curly brackets in Eq. (4) represents a 6-j symbol.[13] The tensor operators $u^{(k)}$ are defined by their reduced matrix elements[14]:

$$(nl\|u^{(k)}\|n'l') = \delta_{nn'}\delta_{ll'}. \qquad (6)$$

For $4f$ electrons in states where the total angular momentum is a good quantum number, the only

part of the Coulomb interaction, Eq. (4), that will be relevant for our calculation of the quadrupole scattering contribution to the anisotropic magnetoresistance is the quadrupole-quadrupole interaction

$$H_2 = (\sqrt{\tfrac{2}{3}})(2F^2 - \tfrac{9}{7}G^1 + \tfrac{11}{42}G^3 - \tfrac{125}{462}G^5)u_a^{(2)} \cdot u_b^{(2)} . \quad (7)$$

We note in passing that there are exchange as well as direct contributions to this coupling. Interaction (7) is for one $4f$ electron. The interaction for the configuration $4f^n$-$5d$ is arrived at simply by replacing $u^{(2)}(i)$ by

$$\sum_{i=1}^{n} u^{(2)}(i) .$$

This operator can be written in terms of the total angular momentum J of the RE ion, e.g.,

$$\sum_{i=1}^{n} u^{(2)}(i) = p O^{(2)}(\vec{J}) , \quad (8)$$

where

$$p = \left(J \| \sum_{i=1}^{n} u^{(2)}(i) \| J \right) \Big/ (J \| O^{(2)} \| J)$$

and the double bars represent a reduced matrix element. We define the tensor operator $O^{(2)}(\vec{J})$ by the following reduced matrix element:

$$(J \| O^{(2)} \| J) = \frac{1}{4} \left(\frac{2(2J+3)!}{3(2J-2)!} \right)^{1/2} . \quad (9)$$

The ratio p can be directly calculated by using coefficients of fractional parentage, and has been given by Kasuya and Lyons[15] for the second half of the RE series as

$$p = \frac{2}{3\sqrt{70}} \frac{L(S - \tfrac{7}{4})}{J(J - \tfrac{1}{2})} . \quad (10)$$

The exchange integrals have been determined by Freeman and Mallow[11] from Hartree-Fock calculations, but the Coulomb integral F^2 was determined from experimental data presented by Condon and Shortley for the $4f$-$5d$ terms in La^+.[16] From these data we find[17]

$$F^2(4f, 5d) \simeq 12\,600\,\text{cm}^{-1} . \quad (11)$$

By using the mean values of the exchange integrals appropriate for the heavy rare earths, i.e.,

$$G^1(4f, 5d) \simeq 10\,200\,\text{cm}^{-1} ,$$
$$G^3(4f, 5d) \simeq 8\,500\,\text{cm}^{-1} , \quad (12)$$
$$G^5(4f, 5d) \simeq 6\,500\,\text{cm}^{-1} ,$$

we find that the quadrupole-quadrupole interaction between the $4f^n$ shell and the $5d$ electron is

$$H_2 = A_2 \frac{L(S - \tfrac{7}{4})}{J(J - \tfrac{1}{2})} O^2(\vec{J}) \cdot u^{(2)}(d) , \quad (13)$$

with

$$A_2 = 814\,\text{cm}^{-1} .$$

The matrix elements between $5d$ states that are relevant for calculating the anisotropic magnetoresistance are given as

$$\langle m | H_2 | m \rangle = \tfrac{1}{2} (\sqrt{\tfrac{3}{35}}) A_2 \frac{L(S - \tfrac{7}{4})}{J(J - \tfrac{1}{2})} (m^2 - 2)$$

$$\times \left(J_z^2 - \frac{J(J+1)}{3} \right) . \quad (13a)$$

For the determination of the negative isotropic magnetoresistance we have to consider the spin-dependent $k = 0$ term in Eq. (4), i.e.,[10]

$$H_0 = -\tfrac{2}{35}(3G^1 + \tfrac{4}{3}G^3 + \tfrac{50}{33}G^5) \vec{s} \cdot \vec{S} , \quad (14)$$

where

$$S = \sum_{i=1}^{n} s_i .$$

By using the exchange integrals given in Eq. (12) we find

$$H_0 = -A_0 \vec{s} \cdot \vec{S} , \quad (14a)$$

with

$$A_0 = 2950\,\text{cm}^{-1} .$$

To calculate the contribution of skew scattering to the Hall effect we have to consider the spin-independent part of Eq. (4) with $k = 1$. The spin-independent term with $k = 3$ in Eq. (4) can also contribute to the Hall effect, but it is shown in Appendix B that it does not contribute to the *initial* Hall coefficient measured by Fert and Friederich.[3] Evaluating the coefficients in Eq. (4) for $k = 1$, we find that the spin-independent part is

$$H_1 = -(3/\sqrt{280})(4G^1 + \tfrac{2}{3}G^3 - \tfrac{50}{33}G^5)u_a^{(1)} \cdot u_b^{(1)} . \quad (15)$$

From the definition, Eq. (6), of the unit tensors we find

$$u^{(1)} = \vec{l}/(l \| \vec{l} \| l) = [l(l+1)(2l+1)]^{-1/2}\vec{l} , \quad (16)$$

so that the $4f$-$5d$ interaction can immediately be written as

$$H_1 = -\tfrac{1}{280}(4G^1 + \tfrac{2}{3}G^3 - \tfrac{50}{33}G^5) \vec{L} \cdot \vec{l} , \quad (17)$$

where

$$\vec{L} \equiv \sum_{i=1}^{n} \vec{l}_i$$

is the orbital angular momentum of the $4f^n$ shell and $\vec{l}$ is the orbital angular momentum of the $5d$ electron.

By using the mean values of the exchange integrals for the heavy rare earths, Eqs. (12), we find

$$H_1 = -A_1 \vec{L} \cdot \vec{l} , \quad (18)$$

with

$$A_1 = 130 \, \text{cm}^{-1}.$$

B. Contribution to the scattering potential from 4f-conduction-electron interaction

We write the scattering potential of a trivalent RE impurity in a monovalent metal as

$$V = V_0 + v(\vec{J}).$$

The first term, V_0, is the spherical term which attracts about two electrons, mostly into $5d$ and $6s$ states. The second term, $v(\vec{J})$, is the Coulomb (direct and exchange) interaction of the conduction electrons with the $4f$ electrons and depends on the $4f$ angular momentum $\vec{J}$. The spherical $\vec{J}$-independent part of the Coulomb interaction is included in V_0. The first term is an order of magnitude larger than the second and comparable to the conduction-electron energy. Therefore this first term should not be treated in a Born approximation, but rather in terms of phase shifts of the partial waves. The effect of the second term is then calculated in the first Born approximation; i.e., we write the T matrix as

$$T_{\vec{k},\vec{k}'}(\vec{J}) = T^{(0)}_{\vec{k},\vec{k}'} + \langle \vec{k}'^{(-)} | v(\vec{J}) | \vec{k}^{(+)} \rangle, \qquad (19)$$

where $|\vec{k}^{(+)}\rangle$ and $|\vec{k}^{(-)}\rangle$ are the outgoing and incoming phase-shifted waves.

The matrix elements of $T^{(0)}$ as a function of the phase shifts are given as[18]

$$T^{(0)}_{\vec{k}\sigma,\vec{k}'\sigma'} = -\frac{4\delta\sigma\sigma'}{N(E_F)} \sum_{l,m} e^{i\eta_l} (\sin\eta_l) Y^*_{lm}(\Omega\vec{k}) Y_{lm}(\Omega\vec{k}'), \qquad (20)$$

where $N(E_F)$ is the density of states at the Fermi level per unit volume and for one spin direction. The phase shifts η_l are related to the lth partial waves of the screening charge by the Friedel sum rule

$$\eta_l = \frac{\pi}{2(2l+1)} Z_l, \qquad (21)$$

and

$$\sum_l Z_l \cong 2$$

for a trivalent impurity in a monovalent noble metal. In our calculation of the magnetoresistance we will take $Z_0 = 1$ ($6s$) and $Z_2 = 1$ ($5d$), so that

$$T^{(0)}_{\vec{k}\sigma,\vec{k}'\sigma'} = -\frac{\delta_{\sigma\sigma'}}{N(E_F)} \left(\frac{1}{\pi} e^{i\eta_0} \sin\eta_0 + 4e^{i\eta_2}(\sin\eta_2) \right.$$
$$\left. \times \sum_m Y^*_{2m}(\Omega\vec{k}) Y_{2m}(\Omega\vec{k}') \right), \qquad (22)$$

with, according to Eq. (21), $\eta_0 = \frac{1}{2}\pi$ and $\eta_2 = \frac{1}{10}\pi$.

Here we have neglected the small p-wave phase shift. However, the p-wave phase shift has to be considered in our calculation of the skew scattering.

If we assume that the $5d$ states are split by the cubic crystal field of the surroundings and only the t_{2g} levels are occupied,[8-10] the $l = 2$ terms in the $T^{(0)}$ matrix Eq. (22) should be replaced by

$$4e^{i\eta_{2t}}(\sin\eta_{2t}) \sum_{\alpha=1,2,3} Y_\alpha(\Omega\vec{k}) Y_\alpha(\Omega\vec{k}'), \qquad (22a)$$

where $\eta_{2t} = \frac{1}{6}\pi$ and the $Y_\alpha(\Omega)$ are Kubic harmonics,[19] i.e., basis functions of the representation $t_{2g}(\Gamma_{5g})$ made up from the second-rank spherical harmonics

$$Y_1 = -(i/\sqrt{2})(Y_{2,2} - Y_{2,-2}),$$
$$Y_2 = (i/\sqrt{2})(Y_{2,1} + Y_{2,-1}), \qquad (23)$$
$$Y_3 = -(1/\sqrt{2})(Y_{2,1} - Y_{2,-1}).$$

These harmonics are defined to be real, i.e., $Y^*_\alpha = Y_\alpha$.

To proceed with the derivation of the $4f$-conduction-electron interaction, we assume that the leading contribution to the matrix elements of $v(\vec{J})$ in Eq. (19) comes from the $5d$ atomic wave functions mixed in the perturbed waves $|k^{(+)}\rangle$ and $|k^{(-)}\rangle$. This follows from the fact that the wave functions of the $5d$ electrons are far more localized about the $4f$ shell than the spherical Bessel functions $j_l(k_F r)$ and the $6s$ wave functions. According to Friedel's theory of the nonmagnetic virtual bound states,[20] the admixture of the $5d$ wave functions in an outgoing $|k^{(+)}\rangle$ or incoming $|k^{(-)}\rangle$ plane wave is written as

$$|k^{(\pm)}\rangle_{5d} = \sum_{m=-2}^{2} C^\pm_m(\vec{k}) |m\rangle, \qquad (24)$$

where

$$C^\pm_m(\vec{k}) = e^{\pm i\eta_2}(\sin\eta_2) \frac{\langle d | V_0 | k \rangle}{\Delta} Y^*_{2m}(\Omega\vec{k}), \qquad (25)$$

Δ is the half width of the VBS, and $|m\rangle$ are the atomic states.

If the $5d$ states are split in the crystal field of the surrounding matrix so that only the t_{2g} states are occupied, Eqs. (24) and (25) are written as

$$|k^{(\pm)}\rangle_{t_{2g}} = \sum_{\alpha=1,2,3} C^\pm_\alpha(\vec{k}) |\alpha\rangle, \qquad (24a)$$

where

$$C^\pm_\alpha(\vec{k}) = e^{\pm i\eta_{2t}}(\sin\eta_{2t}) \frac{\langle d | V_0 | k \rangle}{\Delta} Y_\alpha(\Omega\vec{k}), \qquad (25a)$$

and $|\alpha\rangle$ are the $5d$ atomic states written in terms of the Kubic harmonics, Eq. (23).

Now the matrix elements of $v(\vec{J})$ in Eq. (19) can

be written as

$$dT_{\vec{k}\sigma,\vec{k}'\sigma'} \equiv \langle \vec{k}'^{(-)},\sigma' | v(\vec{J}) | \vec{k}^{(+)},\sigma \rangle$$

$$= \sum_{mm'} C_{m'}^{-}(\vec{k}')^* C_m^{+}(\vec{k}) \langle m',\sigma' | v(\vec{J}) | m,\sigma \rangle .$$

(26)

By using Eq. (25) for the coefficients $C_m^{\pm}$ and by using the relation

$$|\langle k | V_0 | d \rangle|^2 = 4\Delta/N(E_F) ,$$

we find

$$dT_{\vec{k}\sigma,\vec{k}'\sigma'} = \frac{4e^{2i\eta_2}\sin^2\eta_2}{\Delta N(E_F)}$$

$$\times \sum_{m,m'} \langle m',\sigma' | v(\vec{J}) | m,\sigma \rangle$$

$$\times Y_{2m}^*(\Omega_{\vec{k}}) Y_{2m'}(\Omega_{\vec{k}'}) . \qquad (27)$$

In the case of a t_{2g} level instead of the $5d$ we find

$$dT_{\vec{k}\sigma,\vec{k}'\sigma'} = \frac{4e^{2i\eta_{2t}}\sin^2\eta_{2t}}{\Delta_t N(E_F)}$$

$$\times \sum_{\alpha\alpha'} \langle \alpha'\sigma' | v(\vec{J}) | \alpha\sigma \rangle$$

$$\times Y_\alpha(\Omega_{\vec{k}}) Y_{\alpha'}(\Omega_{\vec{k}'}) . \qquad (27a)$$

We can think of these first-order corrections to the T matrix, Eqs. (27) and (27a), as resulting from an effective Coulomb interaction between the conduction and $4f$ electrons. In the case where the $5d$ levels are not split, the effective potential is written as

$$v_{\text{eff}}(\vec{J}) = \frac{4e^{2i\eta_2}\sin^2\eta_2}{\Delta N(E_F)}$$

$$\times \sum_{mm'\vec{k}\vec{k}'} \langle m',\sigma' | v(\vec{J}) | m,\sigma \rangle$$

$$\times Y_{2m}^*(\Omega_{\vec{k}}) Y_{2m'}(\Omega_{\vec{k}'}) a_{\vec{k}'\sigma'}^\dagger a_{\vec{k}\sigma} , \qquad (28)$$

where $a_{\vec{k}\sigma}^\dagger(a_{\vec{k}\sigma})$ are creation (annihilation) operators of plane waves. For example, the spin-dependent $k=0$ term, Eq. (14), of the $4f$-$5d$ interaction yields a contribution to the effective potential which is equivalent to the isotropic exchange term, Eq. (2). If we take terms of the $4f$-$5d$ interaction, Eq. (4) with $k\neq0$, the matrix elements involved in Eq. (28) depend on m and m', and we obtain anisotropic contributions to the effective potential, i.e., contributions which depend on the orientation of $\vec{k}$ and $\vec{k}'$ with respect to the $4f$ moment. In the following section we shall successively calculate the contribution to v_{eff} from the terms H_2, H_0 and H_1 of the $4f$-$5d$ interaction.

III. CALCULATION OF THE COEFFICIENTS OF MAGNETOTRANSPORT AND COMPARISON WITH EXPERIMENTS

A. Anisotropic magnetoresistance

By introducing the matrix elements of the quadrupolar $4f$-$5d$ term, Eq. (13a), in Eq. (27) we obtain the following contribution to the T matrix:

$$dT_{\vec{k}\vec{k}'}^Q = 2\pi e^{2i\eta_2}\frac{D^{(2)}}{N}\left(J_z^2 - \frac{J(J+1)}{3}\right)$$

$$\times \sum_m (m^2-2) Y_{2m}^*(\Omega_{\vec{k}}) Y_{2m}(\Omega_{\vec{k}'}) , \qquad (29)$$

with an effective coefficient for the quadrupole interaction of

$$D^{(2)} = \frac{L(S-\tfrac{7}{4})}{J(J-\tfrac{1}{2})} d^{(2)}$$

$$= \frac{L(S-\tfrac{7}{4})}{J(J-\tfrac{1}{2})} \frac{1}{\pi} (\sqrt{\tfrac{3}{35}}) \frac{(\sin^2\eta_2)A_2}{\Delta n(E_F)} , \qquad (30)$$

where $n(E_F)$ is the density of states at the Fermi level per atom and per spin direction, and N is the number of atoms per unit volume. The resulting contribution to the resistivity anisotropy, after Fert et al.,[4] is

$$\frac{\rho_\parallel - \rho_\perp}{\rho_0} = 6\pi n(E_F)D^{(2)}\frac{\sin\eta_2\cos\eta_2}{\sin^2\eta_0 + 5\sin^2\eta_2}$$

$$\times \left(\langle\langle J_z^2\rangle\rangle - \frac{J(J+1)}{3}\right) , \qquad (31)$$

where $\langle\langle J_z^2\rangle\rangle$ is a thermal and polycrystal average of the component of $\vec{J}$ in the field direction.

From XPS measurements the half width of the $5d$ VBS of Pt in Ag or of the $4d$ VBS of Pd in Au and Ag is about 0.5 eV.[21] Optical measurements on Ag:Pd give a somewhat smaller value: $\Delta = 0.25$ eV.[22] Other optical measurements give $\Delta = 0.4$ eV for the half-width of the $3d$ VBS of Ti in Ag.[23] For the $5d$ VBS of RE impurities only thermoelectric data[6] exist. From Fig. 8 of Ref. 6 and by assuming $Z_0 \sim Z_2 \sim 1$, one finds $\Delta \simeq 0.2$ eV; without an *a priori* assumption on the screening charges, one finds that Δ is certainly smaller than 0.86 eV. Thus there is some scatter of the results, but the half width Δ generally amounts to a few tenths of an eV. We shall assume that the value of Δ is 0.5 eV; by taking $n(E_F) = 0.15$ states/(eV spin atom) and $\eta_2 = \frac{1}{10}\pi$ ($Z_2 \simeq 1$), we find from Eq. (30)

$$d^{(2)} = 0.012 \text{ eV} .$$

For Ho impurities ($S=2$, $L=6$), we obtain for the characteristic energy of the quadrupole interaction

$$E_{\text{qd}} = 5L(S-\tfrac{7}{4})d^{(2)} = 0.09 \text{ eV} .$$

The experimental values[4] derived from the anisotropic magnetoresistance of Au:Ho alloys are $d^{(2)}$ $= 0.020$ eV and $E_{qd} = 0.15$ eV. Thus, we see that our model—without crystal-field splitting of the $5d$ states—yields a quadrupolar coupling somewhat smaller than the experimental one; i.e., our model predicts for Au:Ho alloys an anisotropic magnetoresistance smaller than that observed.

When we take into account the crystal-field splitting of the $5d$ states so that only the t_{2g} states are occupied, we find for the quadrupolar term of the T matrix [see Eqs. (13) and (27a)]

$$dT^Q_{\vec{k}\sigma\vec{k}'\sigma} = 4e^{2i\eta_{2t}} \frac{(\sin^2\eta_{2t})A_2}{\Delta_t N(E_F)} \frac{L(S - \frac{7}{4})}{J(J - \frac{1}{2})}$$

$$\times \sum_{\alpha\alpha'm} (-1)^m O^2_m(J)\langle \alpha' | u^{(2)}_{-m} | \alpha \rangle$$

$$\times Y_{\alpha'}(\Omega_{\vec{k}'})Y_\alpha(\Omega_{\vec{k}}). \tag{32}$$

For this case the magnetoresistance has not been calculated by Fert et al.[4] To obtain the resistivity for the current in the direction of a unit vector $\vec{u}$ and for elastic collisions we use the expression[4]

$$\rho_{\vec{u}} = \frac{1}{2}\left(\frac{\hbar}{8\pi^3 ne}\right)^2 \int \left(-\frac{\partial f^0}{\partial \epsilon_k}\right)(\vec{k}\cdot\vec{u})$$

$$\times [(\vec{k} - \vec{k}')\cdot\vec{u}]w_{\vec{k}\vec{k}'}d\vec{k}\,d\vec{k}', \tag{33}$$

where

$$w_{\vec{k}\vec{k}'} = \frac{2\pi}{\hbar}|T^{(0)}_{\vec{k}\sigma,\vec{k}'\sigma} + dT^Q_{\vec{k}\sigma,\vec{k}'\sigma}|^2\delta(\epsilon_k - \epsilon_{k'}), \tag{34}$$

and n is the number of conduction electrons per unit volume for one spin direction. As we have seen in Appendix C of the preceding paper,[4] Eq. (33) gives the anisotropy of the magnetoresistance correct to first order in the anisotropy of the scattering potential.

We calculate $\rho_{\vec{u}}$ in Appendix A by limiting the development of $w_{\vec{k}\vec{k}'}$ to terms of first order in dT^Q. By comparing the values of $\rho_{\vec{u}}$ for $\vec{u}$ parallel and perpendicular to the field direction z and by averaging over all field directions with respect to the crystal axes, we find for the resistivity anisotropy of a polycrystal

$$\frac{\rho_{\parallel} - \rho_{\perp}}{\rho_0} = \frac{18}{7}\left(\sqrt{\frac{3}{35}}\right)\frac{\cos\eta_{2t}\sin^3\eta_{2t}}{\sin^2\eta_0 + 3\sin^2\eta_{2t}}$$

$$\times \frac{L(S - \frac{7}{4})}{J(J - \frac{1}{2})}\frac{A_2}{\Delta_t}\left(\langle\langle J_z^2\rangle\rangle - \frac{J(J+1)}{3}\right). \tag{35}$$

For Ho^{3+} ($L = 6, S = 2, J = 8$) in gold, the crystal-field parameters have been extracted from the field dependence of the magnetoresistance, and are[4]

$x = -0.35$, $C_4 = -20$ K.

From these parameters and for $H = 35$ kG and $T = 1.2$ K one finds[4]

$$\langle\langle J_z^2\rangle\rangle - \tfrac{1}{3}J(J+1) = 24.2.$$

When we use this value together with $\eta_{2t} = \frac{1}{6}\pi$ ($Z_2 = 1$), $\Delta_t = 0.5$ eV, and $A_2 = 814$ cm^{-1}, we find

$$(\rho_{\parallel} - \rho_{\perp})/\rho_0 = 0.0057. \tag{36}$$

The experimental value for Ho impurities in gold at 36 kG and 1.2 K is 0.0065. The agreement between the calculated and experimental values is much better than in the model without crystal-field splitting of the $5d$ states,

$$(\rho_{\parallel} - \rho_{\perp})/\rho_0 = 0.0041. \tag{36a}$$

This tends to confirm the model[8-10] in which the $5d$ electron exists in a t_{2g} VBS.

B. Negative isotropic magnetoresistance

The contribution of the isotropic exchange term, Eq. (14a), to the effective potential, Eq. (28), is

$$V^{exch}_{eff}(\vec{J}) = -2\pi(g_J - 1)e^{2i\eta_2}\Gamma^{(2)}/N$$

$$\times \sum_{\vec{k}\vec{k}'m} Y^*_{2m}(\Omega_{\vec{k}})Y_{2m}(\Omega_{\vec{k}'})$$

$$\times [(a^\dagger_{\vec{k}+}a_{\vec{k}+} - a^\dagger_{\vec{k}'-}a_{\vec{k}-})J_z$$

$$+ a^\dagger_{\vec{k}'+}a_{\vec{k}-}J^- + a^\dagger_{\vec{k}'-}a_{\vec{k}+}J^+], \tag{37}$$

with an effective coefficient of isotropic exchange

$$\Gamma^{(2)} = (\sin^2\eta_2)A_0/\pi\Delta n(E_F).$$

By using $\eta_2 = \frac{1}{10}\pi, A_0 = 2950$ cm^{-1}, $\Delta = 0.5$ eV, $n(E_F) = 0.15$ states/eV spin atom, we find

$$\Gamma^{(2)} = 0.148 \text{ eV}.$$

The experimental value[4] derived from the isotropic part of the magnetoresistance of Au:Ho alloys is smaller:

$$\Gamma^{(2)} = 0.042 \text{ eV}.$$

Including the crystal-field splitting of the $5d$ VBS in the calculation of the magnetoresistance does not improve the agreement.

C. Hall effect

The expression for the contribution of the skew scattering to the Hall resistivity has been previously derived, and is given as[3]

$$\rho_{xy} = -\frac{1}{2}\left(\frac{\hbar}{8\pi^3 ne}\right)^2 \int \left(-\frac{\partial f^0}{\partial\epsilon_k}\right)(\vec{k}\cdot\vec{u})$$

$$\times (\vec{k}'\cdot\vec{v})w^4_{\vec{k}\sigma\vec{k}'\sigma}\,d\vec{k}\,d\vec{k}', \tag{38}$$

where $\hat{u}$ and $\hat{v}$ are unit vectors in the directions x and y, and where $w^a_{\vec{k}\sigma\vec{k}'\sigma}$ is the *antisymmetric* part of the scattering probability $w_{\vec{k}\sigma\vec{k}'\sigma}$,

$$w_{\vec{k}\sigma\vec{k}'\sigma} = (2\pi/\hbar)|T^{(0)}_{\vec{k}\sigma,\vec{k}'\sigma} + dT_{\vec{k}\sigma,\vec{k}'\sigma}|^2\delta(\epsilon_k - \epsilon_{k'}), \quad (39)$$

where $T^{(0)}$ is given by Eq. (20) and dT by Eq. (27) or (27a). Equation (38) represents the contribution from non-spin-flip (elastic) collisions, which has been shown to be the leading contribution for noble metals with RE impurities[3]; Eq. (38) is also based on the assumption that the spin-up and spin-down electrons carry equal currents. Since the integral of Eq. (38) contains

$$(\vec{k}\cdot\vec{u})(\vec{k}'\cdot\vec{v}) = \tfrac{2}{3}(\pi/i)kk'[Y_{1,1}(\Omega_{\vec{k}}) - Y_{1,-1}(\Omega_{\vec{k}})]$$

$$\times [Y_{1,1}(\Omega_{\vec{k}'}) + Y_{1,-1}(\Omega_{\vec{k}'})], \quad (40)$$

the only parts of the probability that contribute to the Hall resistivity are those for which the conduction-electron variables transform as rank-1 spherical harmonics. If we consider the $5d$ VBS unsplit, the only part of the $4f$-$5d$ Coulomb interaction that contributes to the Hall resistivity is H_1, Eq. (18). The principal contribution to the transition probability $w_{\vec{k}\vec{k}'}$, Eq. (39), is $T^{(0)}dT^*$ $+ T^{(0)*}dT$. Since the harmonics in $dT_{\vec{k}\vec{k}'}$, Eq. (27) [with Eq. (18) for $v(\vec{J})$], are even and the harmonics in Eq. (40) are odd, we must consider the terms with odd l in $T^{(0)}$, Eq. (20), and we shall assume that there is a finite p-wave phase shift $\eta_1 \neq 0$. Upon placing Eq. (18) in Eq. (27) together with Eq. (20) with $l=1$ in Eq. (39), we obtain the antisymmetric part of the scattering probability, and performing the indicated integrations, we find that the skew scattering contribution to the Hall angle is (see Appendix A)

$$\phi = \frac{\rho_{xy}}{\rho_0} = \frac{6A_1}{\Delta} \frac{\sin^2\eta_2 \sin(2\eta_2 - \eta_1)\sin\eta_1}{\sin^2\eta_0 + 5\sin^2\eta_2}\langle L_z\rangle. \quad (41)$$

In the low-field–high-temperature limit the expectation value of the orbital angular momentum of the $4f$ electrons is

$$\langle L_z\rangle = g_J(2 - g_J)J(J+1)\mu_B H/3k_B T,$$

and the initial Hall coefficient $[R = (\rho_{xy}/H)_{H\to 0}]$ is written as

$$R = a_1\rho_0/T, \quad (42)$$

with

$$a_1 = \frac{2A_1\mu_B}{\Delta k_B} \frac{\sin^2\eta_2 \sin(2\eta_2 - \eta_1)\sin\eta_1}{\sin^2\eta_0 + 5\sin^2\eta_2}$$

$$\times g_J(2 - g_J)J(J+1). \quad (43)$$

The major difficulty in evaluating Eq. (43) is that the amount of p-wave screening Z_1 is poorly known.[24] It should be much less than the s- and d-wave

screening and we crudely assume $Z_1 = 0.1$, so that $\eta_1 = \tfrac{1}{60}\pi$. By using $A_1 = 130$ cm^{-1} and the same values of Δ, η_0, and η_2 as before we obtain

$$a_1 = 0.80\times 10^{-8}g_J(2 - g_J)J(J+1) \text{ K/G}. \quad (44)$$

Hall-effect measurements on gold and silver containing RE impurities have shown that, in the limit $H/T \to 0$, the contribution of the rare earths to the Hall coefficient is the sum of two terms $a_1(\rho_0/T)$ and $a_2(\rho_0/T)$ which vary across the RE series as $g_J(2 - g_J)J(J+1)$ and $g_J(g_J - 1)J(J+1)$, respectively.[5] The second term is accounted for by the spin-orbit coupling of the conduction electrons. When we compare our result, Eq. (44), with the magnitude of the first term,

$$a_1 = 0.34\times 10^{-8}g_J(2 - g_J)J(J+1) \text{ K/G}$$

for gold-based alloys

$$= 0.43\times 10^{-8}g_J(2 - g_J)J(J+1) \text{ K/G}$$

for silver-based alloys,

we find that it is at least two times too large. It should be kept in mind that our calculated value depends on our estimate of η_1; if we lowered this value, we could obtain agreement with experiment.

Finally, if we consider that the $5d$ electron exists in only the t_{2g} states, then we must use Eq. (27a), and we find that the skew scattering contribution is reduced (see Appendix A):

$$R = a_1\rho_0/T,$$

with

$$a_1 = \frac{2A_1\mu_B}{5\Delta k_B} \frac{\sin^2\eta_{2t} \sin(2\eta_{2t} - \eta_1)\sin\eta_1}{\sin^2\eta_0 + 3\sin^2\eta_{2t}}$$

$$\times g_J(2 - g_J)J(J+1). \quad (43a)$$

In this case the reduction due to the projection of the angular momentum on the t_{2g} states outweighs the increase due to the larger phase shifts η_{2t}. Therefore we find a smaller estimate for the Hall resistivity when we consider a t_{2g} VBS:

$$a_1 = 0.54\times 10^{-8}g_J(2 - g_J)J(J+1) \text{ K/G} \quad (44a)$$

Although this result is closer to that found from the experimental data than the previous one, Eq. (44), it is still too large.

When we consider the $5d$ electron in t_{2g} states, there is an additional contribution to the Hall resistivity from the $4f$-$5d$ interaction H_3, i.e., from the spin-independent part of Eq. (4) with $k=3$. This occurs because the projection of the harmonics Y_{3m} on the t_{2g} manifold contains a term that transforms under the cubic group symmetry as Γ^4, and this term contributes to the integral, Eq. (38).

We show in Appendix B that this addition contribution does not enter the term in the Hall resistivity which is linear in H/T.

IV. DISCUSSION OF RESULTS

We have calculated the size of the magneto-resistance and the contribution from skew scattering to the Hall effect that is induced by RE impurities in noble metals such as gold or silver. We assumed that these effects arise from the interaction between the $4f$ electrons of the RE and the $5d$ electrons admixed into the conduction-electron states. To obtain the magnitude of the scattering we used the atomic $4f$-$5d$ Coulomb and exchange integrals determined by Freeman and Mallow.[11] In our calculation the width of the $5d$ VBS enters. This width is not well known, but by using a reasonable value of this parameter we obtain a resistivity anisotropy which is close to the experimental value. We are unable to obtain a definite estimate of the skew scattering contribution to the Hall effect because the phase shift η_1 is poorly known. When we used the value of η_1 which corresponds to 0.1 screening p electron, we found the skew scattering contribution was somewhat larger than that extracted from experimental data. In both calculations (resistivity anisotropy and skew scattering) we found that the numerical estimates improved considerably when we considered the $5d$ electrons in a t_{2g} VBS. This result is in agreement with the calculations of Williams and Hirst[8] and of Chow.[9]

From these results we may conclude that the anisotropic parts of the $4f$-$5d$ interactions, i.e., the parts of Eq. (4) with $k \neq 0$, provide a fairly good estimate of the quadrupolar and orbital exchange terms of the scattering potential. A calculation in which the conduction electrons are in pure plane-wave states gives a quadrupolar interaction which is too small by almost two orders of magnitude[15] to explain the anisotropy of the magnetoresistivity. Therefore the admixture of $5d$ electrons (or other localized degenerate orbitals) in the conduction states is essential to account for the magnitude of the anisotropy. One can extend these results and state that, whenever the conduction band has appreciable orbital character, there will be significant anisotropy in the rare-earth-conduction-electron interaction.

Nonetheless, there is one disquieting feature of our model. When we use it to calculate the isotropic exchange between the $4f$ and conduction electrons, we find it is much larger than that extracted from the negative isotropic magnetoresistance of gold-based alloys. It is true that other parts of the $4f$-conduction-electron inter-

action contribute to the isotropic magnetoresistance. However, these contributions only increase the discrepancy between the calculated and observed values. There are at least two possible reasons for this discrepancy. First, it may be that the isotropic spin-dependent part of the $4f$-$5d$ interaction, Eq. (4) with $k = 0$, is wildly overestimated by atomic $4f$-$5d$ exchange integrals. The other possibility is that the half width of the $5d$ VBS is considerably larger than 0.5 eV. This latter possibility is not very appealing, because our agreement for the anisotropic magnetoresistance and skew scattering would be considerably poorer. For the same reason it would not be appropriate to simply scale down all the $4f$-$5d$ atomic intergrals; i.e., by scaling them down to obtain agreement with the data of isotropic magnetoresistance, one just worsens the agreement for the anisotropic effects.

The above observations are reinforced by the calculations of Huang Liu et al.[10] on the g shift Δg and linewidth ΔH of the EPR of RE impurities in noble metals. Their calculation is based on the exchange part of the $4f$-$5d$ interaction Hamiltonian, Eq. (4), and also used atomic integrals for this interaction. They give expressions of Δg for an unsplit VBS and a t_{2g} VBS and of ΔH for only an unsplit VBS.

By using these expressions for erbium and a half-width $\Delta = 0.5$ eV for the VBS we find the $4f$-$5d$ contributions are

$$\Delta g_{calc} = 0.218, \quad (\Delta H/\Delta T)_{calc} = 119.2 \text{ G/K}$$

for an unsplit VBS, and

$$\Delta g_{calc} = 0.228$$

for a t_{2g} VBS.

The experimental data for Er^{+3} in gold and silver are

$$\Delta g_{expt} \approx 0.03, \quad (\Delta H/\Delta T)_{expt} = 2.7 \text{ G/K}$$

for Au:Er,[25,26] and

$$\Delta g_{expt} \simeq 0.07, \quad (\Delta H/\Delta T)_{expt} = 10.5 \text{ G/K}$$

for Ag:Er.[25,27] By using the expressions of Huang Liu et al.[10] for Dy impurities with $\Delta = 0.5$ eV we obtain

$$(\Delta H/\Delta T)_{calc} = 240.8 \text{ G/K},$$

and from the experimental data for Dy^{3+} in silver we find[28]

$$(\Delta H/\Delta T)_{expt} = 18.5 \text{ G/K}.$$

On comparing the experimental data to the calculated values we note that the estimates are far too large (the difference is greater for the linewidth because the square of the $4f$-$5d$ interaction enters

this expression, whereas this enters linearly for the g shift). The major contribution to these quantities comes from the *isotropic* portion of the $4f$-$5d$ exchange interaction (see Tables 4 and 5 of Ref. 10). Therefore we are led to the same conclusion mentioned above.

From the above we can state that the $4f$-$5d$ atomic integrals provide a fair estimate of the anisotropic portion of the $4f$-conduction-electron interaction for rare earths in noble metals, but they greatly overestimate the isotropic portion.

ACKNOWLEDGMENTS

APPENDIX A

The integrations that enter the magnetoresistivities are straightforward when the current and magnetic field are along principal axes of the cubic crystal. However, for polycrystalline samples the directions of the current and field assume all orientations when viewed from the local crystal-field axes. In other words, in the case of polycrystals it is necessary to perform a powder average. Here we show how this is done.

The expression for determining the anisotropy of the magnetoresistance is given by Eq. (33). As mentioned in the text, we limit our calculation to terms that are first order in dT [see Eq. (34)]. Since we assume there is negligible screening charge with p character about the rare-earth ion, i.e., $\eta_1 \cong 0$, the integrand with $(\vec{k} \cdot \hat{u})$ $(\vec{k}' \cdot \hat{u})$ vanishes upon integration. By using Eq. (22) for T^0 and Eq. (27) together with Eq. (13) for dT we find that the angular integrations entering the magneto-resistivity are

$$\sum_{m_1 m_2 m_3} (-1)^{m_3} O^2_{m_3}(J) \langle 2m_2 | u^2_{-m_3} | 2m_1 \rangle$$

$$\times \sum_{m_4} \int Y_{2m_2}(\Omega_{\vec{k}'}) Y^*_{2m_4}(\Omega_{\vec{k}'}) d\Omega_{\vec{k}'}$$

$$\times \int Y^*_{2m_1}(\Omega_{\vec{k}}) Y_{2m_4}(\Omega_{\vec{k}})(\hat{k} \cdot \hat{u})^2 d\Omega_{\vec{k}} . \quad (A1)$$

We can write the scalar product $(\hat{k} \cdot \hat{u})^2$ as

$$(\hat{k} \cdot \hat{u})^2 = \tfrac{2}{3}(\tfrac{4}{5}\pi)^{1/2} Y_{20}(\hat{u}) + \tfrac{1}{3}, \quad (A2)$$

where the spherical harmonic is referred to the direction of the current $\hat{u}$. If we choose this form of writing $(\hat{k} \cdot \hat{u})^2$, we must write the other spherical harmonics on the same axes. This means that the matrix $\langle 2m_2 | u^2_{-m_3} | 2m_1 \rangle$ is also evaluated with the axis of quantization parallel to the current $\hat{u}$. Since we wrote the scalar product $O^2(J) \cdot u^2$ [see Eq. (13)] in the simple form

$$O^2(J) \cdot u^2 = \sum_{m_3} (-)^{m_3} O^2_{m_3}(J) u^2_{-m_3} , \quad (A3)$$

we have chosen the same axes of quantization for the operators O^2 and u^2. This implies that the operator $O^2_{m_3}(J)$ is also quantized along the direction of the current.

The angular integrations in Eq. (A1) are readily evaluated, and are

$$\int Y_{2m_2} Y^*_{2m_4} d\Omega_{\vec{k}'} = \langle 2m_2 | 2m_4 \rangle^* = \delta_{m_2 m_4} , \quad (A4)$$

$$\tfrac{2}{3}(\tfrac{4}{5}\pi)^{1/2} \int Y^*_{2m_1} Y_{2m_4} Y_{20} d\Omega_{\vec{k}}$$

$$= \tfrac{2}{3}(\tfrac{4}{5}\pi)^{1/2} \langle 2m_1 | Y_{20} | 2m_4 \rangle$$

$$= (-)^{m_1+1} \tfrac{2}{3}(\tfrac{10}{7})^{1/2} \begin{pmatrix} 2 & 2 & 2 \\ -m_1 & 0 & m_4 \end{pmatrix} , \quad (A5)$$

and

$$\langle 2m_2 | u^2_{-m_3} | 2m_1 \rangle = (-)^{m_2} \begin{pmatrix} 2 & 2 & 2 \\ -m_2 & -m_3 & m_1 \end{pmatrix}$$

By placing these results in Eq. (A1), summing over the variables m_1, m_2, and m_4, and using the relation

$$\sum_{m_1 m_2} \begin{pmatrix} 2 & 2 & 2 \\ -m_2 & m_1 & -m_3 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ -m_2 & m_1 & 0 \end{pmatrix} = \tfrac{1}{5} \delta_{m_3 0} , \quad (A6)$$

we find the magnetoresistivity along a direction $\hat{u}$ with a magnetic field along another direction $\vec{H}$ is proportional to

$$\rho_{\hat{u}}(\vec{H}) \sim -\tfrac{2}{3}(\tfrac{2}{35})^{1/2} \langle O^2_0(J; \hat{u}) \rangle_{\vec{H}} . \quad (A7)$$

The angular brackets about the operator O^2_0 denote the thermal expectation value of this operator for the rare-earth $4f$ electrons subject to both a cubic crystal field and magnetic field H. The notation $O^2_0(J; \hat{u})$ is used to emphasize that the operator is quantized along the direction of the current. Finally, one arrives at the anisotropy of the magnetoresistance of a single crystal by taking the difference in the resistivities for the magnetic field parallel and perpendicular to the current:

$$\rho_{\hat{u}}(H_{\parallel}) - \rho_{\hat{u}}(H_{\perp})$$
$$\sim -\tfrac{2}{3}(\tfrac{2}{35})^{1/2}[\langle O_0^2(J;\hat{u})\rangle_{\vec{H}_{\parallel}\hat{u}} - \langle O_0^2(J;\hat{u})\rangle_{\vec{H}_{\perp}\hat{u}}] , \tag{A8}$$

where

$$\langle O_0^2 \rangle_{H\perp\hat{u}} = \sum_{m=-2}^{2} (\tfrac{4}{5}\pi)^{1/2} Y_{2m}(\tfrac{1}{2}\pi,\phi)\langle O_m^2 \rangle_{\vec{H}_{\parallel}\hat{u}} .$$

This is the anisotropy for a *single* crystal. If the sample is polycrystalline, one must average Eq. (A8) over all orientations of the crystal-field axes, i.e., perform a powder average on Eq. (A8).

Instead of averaging over all orientations of the crystal-field axes, we can hold these axes fixed and average over all directions of the current and field:

$$\rho_{\parallel} - \rho_{\perp} \sim \langle\langle O_0^2 \rangle\rangle_{\vec{H}\parallel\hat{u}} - \langle\langle O_0^2 \rangle\rangle_{\vec{H}\perp\hat{u}} , \tag{A9}$$

where

$$\langle\langle O_0^2 \rangle\rangle_{\vec{H}\cdot\hat{u}} \equiv \int \langle O_0^2(J;\hat{u})\rangle_{\vec{H}\cdot\hat{u}} \, d\hat{u} .$$

Now the operator $O_0^2(J;\hat{u})$ is referred to the crystal-field axes and is written as

$$O_0^2(J;\hat{u}) = \sum_m D_{m0}^{(2)}(\hat{u}) O_m^2(J) , \tag{A10}$$

where $D_{m0}^{(2)}$ is a matrix element of the rotation operator that takes the direction of the current $\hat{u}$ into the $C_4(z)$ axis of the crystal field.

After powder averaging over a polycrystal, there is no longer any preferred directions other than that of the applied field and the current. Therefore the dependence of the powder-averaged expectation values on the angle between the current and field is given as

$$\langle\langle O_0^2 \rangle\rangle_{\Omega_H} = \sum_m D_{m0}^{(2)}(\Omega_H)\langle\langle O_m^2 \rangle\rangle_{\vec{H}\parallel\hat{u}} = D_{00}^{(2)}(\Omega_H)\langle\langle O_0^2 \rangle\rangle_{\vec{H}\parallel\hat{u}} , \tag{A11}$$

where Ω_H is the angle of $\vec{H}$ relative to $\hat{u}$. We have used the fact that for a powder average only the axial component of the tensor operator exists. For $\Omega_H = \tfrac{1}{2}\pi, \phi$,

$$D_{00}^{(2)}(\tfrac{1}{2}\pi,\phi) = (\tfrac{4}{5}\pi)^{1/2} Y_{20}(\tfrac{1}{2}\pi,\phi) = -\tfrac{1}{2} ,$$

so that one immediately finds that the anisotropy of the resistivity is

$$\rho_{\parallel} - \rho_{\perp} \sim -(\tfrac{2}{35})^{1/2}\langle\langle O_0^2 \rangle\rangle_{\vec{H}\parallel\hat{u}} . \tag{A12}$$

The full expression of the resistivity anisotropy, including all the coefficients which precede the integral over the angles, is given by Eq. (35).

When we calculate the resistivity for the $5d$ electrons in t_{2g} states we must use Eq. (22a) for T^0 and Eq. (32) for dT. To make full use of the cubic symmetry, we write the scalar product $O^2 \cdot u^2$ in

terms of the tensor cubic operators defined by Callen and Callen[19]:

$$O^{(2)} \cdot u^2 = \sum_{\alpha=1}^{5} O_\alpha u_\alpha , \tag{A13}$$

where, for example,

$$O_1 \equiv O_0^2 .$$

We note that in this sum α runs over both representations $t_{2g}(\Gamma_g^5)$ and $E_g(\Gamma_g^3)$. Also, we write $Y_0^2(\hat{u})$ as $Y_1(\hat{u})$. The angular integrations entering the magnetoresistivity are written as

$$\sum_{\alpha=1}^{5} O_\alpha(J) \sum_{i,j,k=1}^{3} \langle \Gamma_i^5 | u_\alpha | \Gamma_j^5 \rangle \langle \Gamma_j^5 | Y_1 | \Gamma_k^5 \rangle \langle \Gamma_k^5 | \Gamma_i^5 \rangle . \tag{A14}$$

We have written the integrations over $\hat{k}$ and $\hat{k}'$ in bracket notation. The difficulty that enters the calculation is that the $5d$-electron crystal-field t_{2g} states $|\Gamma_q^5\rangle$ ($q = i,j,k$) are referred to the cubic axes (of C_4 symmetry), while the operator $Y_1(\hat{u})$ is quantized along $\hat{u}$. Therefore to evaluate the matrix element we must first rotate the harmonic Y_1 so it is quantized along a $C_4(z)$ axis of the cubic crystal field:

$$Y_1(\hat{u}) = \sum_{\alpha=1}^{5} D_{\alpha 1}^{(2)}(\hat{u}) Y_\alpha(\hat{z}) , \tag{A15}$$

where

$$D_{\alpha 1}^{(2)} = \sum_{m=-2}^{2} D_{m0}^{(2)}\langle \alpha | m \rangle ,$$

and $\langle \alpha | m \rangle$ is a matrix element of the transformation from the spherical harmonic to the Kubic-harmonic basis for rank-2 harmonics i.e.,

$$|m\rangle = \sum_{\alpha=1}^{5} \langle \alpha | m \rangle | \alpha \rangle . \tag{A16}$$

By using the Wigner-Eckart theorem we find the integrals in Eq. (A14) can be reduced:

$$\langle \Gamma_i^5 | u_\alpha | \Gamma_j^5 \rangle \equiv A_\alpha(u) \begin{pmatrix} \Gamma^5 & \Gamma^5 & \Gamma^\alpha \\ i & j & p \end{pmatrix} ,$$

$$\langle \Gamma_j^5 | Y_{\alpha'} | \Gamma_k^5 \rangle \equiv A_{\alpha'}(Y) \begin{pmatrix} \Gamma^5 & \Gamma^5 & \Gamma^{\alpha'} \\ j & k & r \end{pmatrix} , \tag{A17}$$

and

$$\langle \Gamma_k^5 | \Gamma_i^5 \rangle = \delta_{ki} ,$$

where

$$A_\alpha(\xi) = \langle \Gamma^5 | | \Gamma_\alpha(\xi) | | \Gamma^5 \rangle .$$

By using the properties of the Clebsch-Gordan coefficients of the *cubic* group, we find

$$\sum_{ij} \begin{pmatrix} \Gamma^5 & \Gamma^6 & \Gamma^\alpha \\ i & j & p \end{pmatrix} \begin{pmatrix} \Gamma^5 & \Gamma^6 & \Gamma^{\alpha'} \\ i & j & r \end{pmatrix} = \delta_{\alpha\alpha'}\delta_{pr}, \quad (A18)$$

so that Eq. (A14) reduces to

$$\sum_{\alpha=1}^{5} O_\alpha(J) D_{\alpha1}^{(2)}(\hat{u}) A_\alpha(u) A_\alpha(Y). \quad (A19)$$

In general, the reduced matrix elements A_α depend on whether Γ^α is Γ^3 or Γ^5. However, when the operators are constructed from rank-2 harmonics and when the Γ^5 states come from d ($l=2$) electrons, one finds

$$A_3(u) = -A_5(u). \quad (A20)$$

This relation has been noticed by Abragam and Bleaney.[29] As the reduced matrix elements of $\Gamma^\alpha(Y)$ differ from those of $\Gamma^\alpha(u)$ only by a constant, we find for our case the fortuitous result that the reduced matrix elements can be placed outside the sum in Eq. (A19), and that the resistivity along the direction $\hat{u}$ is proportional to

$$\rho_{\hat{u}} \sim A_3(u) A_3(Y) \sum_{\alpha=1}^{5} D_{\alpha1}^{(2)}(\hat{u}) O_\alpha(J), \quad (A21)$$

or by using Eq. (A15) we can write this as

$$\rho_{\hat{u}} \sim A_3(u) A_3(Y) O_0^2(J, \hat{u}). \quad (A21')$$

Upon evaluating the reduced matrix elements we find

$$A_3(u) = \sqrt{\tfrac{3}{35}}$$

and $\qquad\qquad\qquad\qquad\qquad$ (A22)

$$A_3(Y) = -(\tfrac{5}{4}\pi)^{1/2}(\tfrac{1}{7}\sqrt{6}).$$

When we add the factor $\tfrac{2}{3}(\tfrac{4}{5}\pi)^{1/2}$ in front of the spherical harmonic in Eq. (A2) and take the thermal average of the operator O_0^2 we find the resistivity, Eq. (A21'), is proportional to

$$\rho_{\hat{u}}(\vec{H}) \sim -\tfrac{2}{7}(\sqrt{\tfrac{2}{35}})\langle O_0^2(J;\hat{u})\rangle_{\vec{H}}. \quad (A23)$$

On comparing this expression to Eq. (A7), we conclude that the effects of the angular integrations entering the resistivity are such as to only reduce it for $5d$ electrons in t_{2g} states by a factor of $\tfrac{3}{7}$. One still has to take the thermal expectation value and powder average of the same operator, i.e., only the O_0^2 that enters the resistivity for an unsplit $5d$ VBS.

By using the above method we can also determine the angular integrations entering the skew scattering contribution to the Hall resistivity, Eq. (38). In the low-field–high-temperature limit the crystal-field levels of the ground $4f^n$ manifold are equally occupied and the expectation value of the orbital angular momentum is calculated as for a free ion. In this limit, the angular momentum points along the direction of the applied field, i.e.,

$$\langle L_m \rangle_{\vec{H}} = \langle L_z \rangle_{\vec{H}} \delta_{mo}. \quad (A24)$$

For free $5d$ electrons we are free to choose our axes of quantization (z) for the harmonics entering Eq. (38). When we choose the z axis parallel to the magnetic field the integrand $(\vec{k}\cdot\hat{u})(\vec{k}'\cdot\hat{v})$ takes on the simple form, Eq. (40), and the angular integrations entering the resistivity can be written as

$$\rho_{xy} = \tfrac{4}{3}\pi \sum_{\substack{m_1 m_2 \\ m_3 m_4}} (-)^{m_4}\langle L_{m_4}\rangle_{\vec{H}}\langle 2m_1|l_{-m_4}|2m_2\rangle$$

$$\times \langle 2m_2|Y_x|1m_3\rangle\langle 1m_3|Y_y|2m_1\rangle, \quad (A25)$$

where

$$Y_x = -(1/\sqrt{2})(Y_{1,1} - Y_{1,-1}) \equiv \sum_m \langle m|x\rangle Y_{1,m}$$

and

$$Y_y = (i/\sqrt{2})(Y_{1,1} + Y_{1,-1}) \equiv \sum_m \langle m|y\rangle Y_{1,m}.$$

By using the Wigner-Eckart theorem and recoupling the angular momenta we find

$$\rho_{xy}(\vec{H}) \sim \tfrac{4}{3}\pi\langle L_z\rangle_{\vec{H}} \begin{Bmatrix} 1 & 1 & 1 \\ 2 & 2 & 1 \end{Bmatrix} (2\|l\|2)$$

$$\times (2\|Y^{(1)}\|1)^2 \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ x & y & z \end{pmatrix},$$

where

$$\begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ x & y & z \end{pmatrix} = \sum_m \langle x|m\rangle \begin{pmatrix} 1 & 1 & 1 \\ m & 0 & -m \end{pmatrix} \langle m|y\rangle.$$

$$(A26)$$

When we evaluate the reduced matrix elements and the $3j, 6j$ symbols we find

$$\begin{Bmatrix} 1 & 1 & 1 \\ 2 & 2 & 1 \end{Bmatrix} = -1/2\sqrt{5},$$

$$(2\|l\|2) = \sqrt{30}, \quad (2\|Y^{(1)}\|1) = (6/4\pi)^{1/2},$$

and

$$\begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ x & y & z \end{pmatrix} = i/\sqrt{6}. \quad (A27)$$

Upon placing these values in Eq. (A26) we find the angular integration part of the Hall resistivity

$$\rho_{xy}(\vec{H}) \sim -i\langle L_z\rangle_{\vec{H}}. \quad (A28)$$

When the $5d$ electrons are in t_{2g} states the angular integrations entering the resistivity are written as

$$\rho_{xy} \sim \frac{4}{3}\pi \sum_{\substack{m_1 m_2 \\ m_3 m_4}} (-)^{m_4} \langle L_{m_4} \rangle_{\hat{\mathrm{H}}} \langle \Gamma_{m_1}^5 | l_{-m_4} | \Gamma_{m_2}^5 \rangle$$

$$\times \langle \Gamma_{m_2}^5 | Y_x(\hat{H}) | \Gamma_{m_3}^4 \rangle \langle \Gamma_{m_3}^4 | Y_y(\hat{H}) | \Gamma_{m_1}^5 \rangle \,.$$

$$(A29)$$

The t_{2g} states have been written in the complex basis notation which is particularly suitable for matrix elements of vector operators. It is difficult to refer everything to the field direction in this case, because the cubic states $\langle \Gamma_m^5 \rangle$ referred to this axis have a complicated form and the explicit evaluation of the matrix elements is not simple. Therefore we refer the states to an axis of C_4 symmetry and rotate the harmonics quantized along the field direction so they are quantized along the axis of C_4 symmetry:

$$Y_p(\hat{H}) \equiv \sum_{m_5} D_{m_5 p}^{(1)}(\hat{H}) \, Y_{m_5}(\hat{z}) \,, \qquad (A30)$$

where

$$D_{m_5 p}^{(1)}(\hat{H}) \equiv \sum_m D_{m_5 m}^{(1)} \langle m \,|\, p \rangle \,,$$

and $p = x, y$. By applying the Wigner-Eckart theorem we find

$$\rho_{xy}(\vec{H}) \sim \frac{4}{3}\pi \sum_{m_4} (-)^{m_4} \langle L_{-m_4} \rangle_{\hat{\mathrm{H}}}$$

$$\times \sum_{m_5 m_6} D_{m_5 x}^{(1)}(\hat{H}) \, D_{m_6 y}^{(1)}(\hat{H})$$

$$\times (\Gamma^5 \| l \| \Gamma^5)(\Gamma^5 \| Y^{(1)} \| \Gamma^4)^2$$

$$\times A(\Gamma^4 \Gamma^5) \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ m_5 & m_6 & m_4 \end{pmatrix} \,. \qquad (A31)$$

To arrive at this we made use of the following relation, which is a generalization of one for $3j$ symbols:

$$\sum_{m_1 m_2 m_3} \begin{pmatrix} \Gamma^5 & \Gamma^4 & \Gamma^5 \\ m_1 & m_4 & m_2 \end{pmatrix} \begin{pmatrix} \Gamma^5 & \Gamma^4 & \Gamma^4 \\ m_2 & m_5 & m_3 \end{pmatrix} \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^5 \\ m_3 & m_6 & m_1 \end{pmatrix}$$

$$= A(\Gamma^4, \Gamma^5) \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ m_5 & m_6 & m_4 \end{pmatrix} \,, \qquad (A32)$$

where A is independent of the partner indices and depends only on the irreducible representations, i.e., Γ^4 and Γ^5. The product of the two matrix elements of the rotation operator can be written as one:

$$\sum_{m_5 m_6} D_{m_5 x}^{(1)}(\hat{H}) \, D_{m_6 y}^{(1)}(\hat{H}) \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ m_5 & m_6 & m_4 \end{pmatrix}$$

$$= \sum_m D_{m_4 m}^{(1)*} \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ x & y & m \end{pmatrix} \,, \qquad (A33)$$

where we used the fact that the matrix

$$\begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ m_5 & m_6 & m_4 \end{pmatrix}$$

is proportional to the $3\text{-}j$ symbol

$$\begin{pmatrix} 1 & 1 & 1 \\ m_5 & m_6 & m_4 \end{pmatrix} \,.$$

When we sum over the indice m_4 in Eqs. (A32) and (A33) we find

$$\sum_{m_4} (-)^{m_4} L_{-m_4} D_{m_4 m}^{(1)*}(\hat{H}) \equiv L_m^*(\hat{H}) \qquad (A34)$$

or the angular momentum operator quantized along the direction of the field. By placing the results, Eqs. (A33) and (A34), in Eq. (A31) and using the relation (A24) we find that the skew scattering contribution to the Hall resistivity for $5d$ electrons in t_{2g} states is proportional to

$$\rho_{xy} \sim \frac{4}{3}\pi \langle L_z \rangle_{\hat{\mathrm{H}}} A(\Gamma^4, \Gamma^5)(\Gamma^5 \| l \| \Gamma^5)$$

$$\times (\Gamma^5 \| Y^{(1)} \| \Gamma^4)^2 \begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ x & y & z \end{pmatrix} \,. \qquad (A35)$$

This result is nearly the same as that found for free $5d$ electrons; the difference is just in the reduced matrix elements and in the factor $A(\Gamma^4, \Gamma^5)$, which is the equivalent of the $6\text{-}j$ symbol in Eq. (A26) for the recoupling of cubic group representations.

To evaluate the reduced matrix elements and the constant A we need to calculate only the matrix elements for one set of values of the indices m_4, m_5, and m_6 in Eq. (A32), and take the indicated sum over the remaining indices m_1, m_2, and m_3. Since we know the value of the Clebsch-Gordan coefficient

$$\begin{pmatrix} \Gamma^4 & \Gamma^4 & \Gamma^4 \\ m_5 & m_6 & m_4 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ m_5 & m_6 & m_4 \end{pmatrix} \,, \qquad (A36)$$

we readily find the constant A. For example, for $m_5 = -m_6 = 1$ and $m_4 = 0$ we find

$$\sum_{m_1 m_2 m_3} \langle \Gamma_{m_1}^5 | l_0 | \Gamma_{m_2}^5 \rangle \langle \Gamma_{m_2}^5 | Y_{11} | \Gamma_{m_3}^4 \rangle \langle \Gamma_{m_3}^4 | Y_{1-1} | \Gamma_{m_1}^5 \rangle = \frac{3}{8\pi} \mathrm{Tr} \begin{pmatrix} -1 & & \\ & 0 & \\ & & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{\tfrac{2}{5}} & 0 & 0 \\ 0 & \sqrt{\tfrac{2}{5}} & 0 \end{pmatrix} \begin{pmatrix} 0 & -\sqrt{\tfrac{2}{5}} & 0 \\ 0 & 0 & -\sqrt{\tfrac{2}{5}} \\ 0 & 0 & 0 \end{pmatrix} = \frac{3}{8\pi}(-\tfrac{2}{5}) \,.$$

$$(A37)$$

By using the value $1/\sqrt{6}$ for the Clebsch-Gordan coefficient, Eq. (A36), it immediately follows that

$$(\Gamma^5 \| l \| \Gamma^5)(\Gamma^5 \| Y^{(1)} \| \Gamma^4)^2 A(\Gamma^4, \Gamma^5) = -(\tfrac{2}{5}\sqrt{6})(3/8\pi).$$
(A38)

When we use Eq. (A27) for the Clebsch-Gordan coefficient, we find

$$\rho_{xy} \sim \tfrac{1}{5}(-i)\langle L_z \rangle_{\bar{H}}.$$
(A39)

We conclude that the angular integrations for the $5d$ electrons in t_{2g} states lead to a Hall resistivity $\tfrac{1}{5}$ that for free $5d$ electrons.

APPENDIX B

In this appendix, we calculate the contributions of H_4 to the anisotropy of the resistivity, Eq. (35), and of H_3 to the Hall resistivity, Eq. (44a). In addition, we show that the spin-dependent part of H_4 gives a small and negligible contribution to the isotropic magnetoresistivity. These interactions contribute only when the $5d$ VBS is split by the crystal field so that the t_{2g} or e_g state is preferentially occupied.

The complete fourth-rank $4f$-$5d$ interaction is readily obtained from Eq. (4) and is

$$H_4 = \alpha_4 u_a^{(4)} \cdot u_b^{(4)} + 4\beta_4 u_a^{(4)} \cdot u_b^{(4)} \vec{S}_a \cdot \vec{S}_b,$$
(B1)

where

$$\alpha_4 = (1/55)^{1/2}[10F^4 - \tfrac{9}{14}(11G^1 + \tfrac{44}{9}G^3 + \tfrac{25}{99}G^5)],$$

and β_4 is obtained by setting $F^4 = 0$ in the expression for α_4. For n equivalent $4f$ electrons this interaction is written as

$$H_4 = a_4 \alpha_4 u_a^{(4)} \cdot U_b^{(4)} + 4b_4 \beta_4 u_a^{(4)} \cdot U_b^{(4)} \vec{S}_a \cdot \vec{S}_b,$$
(B2)

where

$$a_4 \equiv \frac{\left(L \| \sum_{i=1}^{n} u_i^{(4)} \| L\right)}{(L \| U^{(4)} \| L)}$$

and

$$b_4 \equiv \frac{\left(LS \| \sum_{i=1}^{n} u_i^{(4)} \vec{s}_i \| LS\right)}{(L \| U^{(4)} \| L)(S \| \vec{S} \| S)}.$$

For Ho^{3+} we find by using the coefficients of fractional parentage[30] that

$$a_4 = -0.636, \quad b_4 = 0.1595.$$
(B3)

Under spherical symmetry the operator $u^{(4)}$ transforms as a fourth-rank tensor and contributes neither to the anisotropic magnetoresistance nor to the negative isotropic magnetoresistance. However, when the $5d$ electron is in the t_{2g} state, we classify the transformation properties of the operator $u^{(4)}$ according to the cubic group. Under this symmetry the operator $u^{(4)}$ has a "spherical"

part Γ^1 and a "quadrupolar" portion Γ^3 and Γ^5, and an antisymmetric term Γ^4:

$$u^{(4)} \cdot U^{(4)} = \Gamma^1(u^{(4)})\Gamma^1(U^{(4)}) + \sum_{i=1,2} \Gamma_i^3(u^{(4)})\Gamma_i^3(U^{(4)})$$
$$+ \sum_{i=1,2,3} \Gamma_i^4(u^{(4)})\Gamma_i^4(U^{(4)})$$
$$+ \sum_{i=1,2,3} \Gamma_i^5(u^{(4)})\Gamma_i^5(U^{(4)}),$$
(B4)

where

$$\Gamma^1(u^{(4)}) = (\tfrac{7}{12})^{1/2}u_0^{(4)} + (\tfrac{5}{24})^{1/2}(u_4^{(4)} + u_{-4}^{(4)})$$

and
(B5)

$$\Gamma_1^3(u^{(4)}) = (\tfrac{5}{12})^{1/2}u_0^{(4)} - (\tfrac{7}{24})^{1/2}(u_4^{(4)} + u_{-4}^{(4)}).$$

We have not listed the other portions of the decomposition, since they are readily found in Callen and Callen.[19] The expectation values of these operators for the $5d$ electron in t_{2g} states, Eq. (23), are

$$\langle \Gamma^1(u^{(4)}) \rangle_{t_{2g}} = -2/3\sqrt{30},$$
$$\langle \Gamma_1^3(u^{(4)}) \rangle_{t_{2g}} = -\tfrac{1}{3}(\sqrt{\tfrac{2}{21}})(3\bar{l}_z^2 - 2),$$
(B6)

where $\bar{l} = 1$. Therefore, when we project the fourth-rank interaction H_4, Eq. (B2), on the $5d$-t_{2g} states, we find

$$\langle H_4 \rangle_{t_{2g}} = (a_4\alpha_4 + 4b_4\beta_4 \vec{S}_a \cdot \vec{S}_b)$$
$$\times [-(2/3\sqrt{30})\Gamma^1(U_b^{(4)})$$
$$- (\sqrt{\tfrac{2}{21}})(\bar{l}_{za}^2 - \tfrac{2}{3})\Gamma_1^3(U_b^{(4)}) + \cdots].$$
(B7)

The first term in the square brackets is isotropic in the orbital variables and contributes to the isotropic magnetoresistance

$$\langle H_4 \rangle_{t_{2g}}(\Gamma^1) = -A_0' \vec{S}_a \cdot \vec{S}_b,$$
(B8)

where

$$A_0' = (8/3\sqrt{30})b_4\beta_4\Gamma^1(U_b^{(4)}).$$

The size of the contribution from this term is obtained by comparing A_0' to the isotropic exchange constant, Eq. (14a):

$$A_0 = 2950 \text{ cm}^{-1}.$$
(B9)

As the $4f^n$ electrons are in spin-orbit coupled states, we must evaluate $\Gamma^1(U_b^{(4)})$ together with $\vec{S}_b$ in Eq. (B8). We are interested in Ho^{3+} where $J = 8$, and to evaluate $\Gamma^1(U^{(4)})\vec{S}$ we consider the ion in a strong magnetic field so that the state is $|J = 8, M_J = 8\rangle$. Then we find

$$\langle 88 | \Gamma^1(U^{(4)})\vec{S} | 88 \rangle = \frac{1}{2}\left(\frac{3 \times 11}{13 \times 17}\right)^{1/2},$$

in which

$$\langle 88 | \vec{S} | 88 \rangle = 2.$$
(B10)

For this state the interaction H_4 gives a contribution

$$\langle 88 | (H_4)_{t_{2g}} | 88 \rangle = -\frac{1}{2} \left(\frac{3 \times 11}{13 \times 17} \right)^{1/2} A_0' s_z(a) . \quad \text{(B11)}$$

By evaluating β_4 from Eqs. (B1) and (12) and using the value, Eq. (B3) for b_4, we determine A_0' and find

$$\langle H_4 \rangle \cong 198 s_z(a) \text{ cm}^{-1} . \quad \text{(B12)}$$

From the isotropic exchange interaction we find

$$\langle H_0 \rangle \cong -6000 s_z(a) \text{ cm}^{-1} . \quad \text{(B13)}$$

On comparing the two values we see that the interaction H_4 contributes a very small amount to the isotropic exchange field acting on the conduction-electron spins $s_z(a)$ for Ho^{3+}. Therefore its contribution to the isotropic magnetoresistivity of Ho^{3+} can be safely neglected. Parenthetically, it should be added that the constant term in Eq. (B7), i.e.,

$$-(2/3\sqrt{30}) a_4 \alpha_4 \Gamma^1 (U_b^{(4)}) \cong 25 \text{ cm}^{-1},$$

gives a very small contribution to the resistivity ρ_0 proportional to

$$\frac{\langle H_4 \rangle}{\Delta} \cong \frac{25 \text{ cm}^{-1}}{4000 \text{ cm}^{-1}} \cong \frac{1}{200} ,$$

where $\Delta = \frac{1}{2}$ eV is the half width of the $5d$ VBS. This value has to be compared to the leading contribution to the isotropic resistivity, which is proportional to $\sin^2 \eta_0 \cong 1$.

The second term in the square brackets in Eq. (B7) and the other terms transforming according to the Γ^3 and Γ^5 representations, Eq. (B7), together with the spin-independent part $a_4 \alpha_4$, i.e.,

$$\langle H_4 \rangle_{t_{2g}} = a_4 \alpha_4 \sum_{i=1,2} \langle \Gamma_i^3 (u_a^{(4)}) \rangle_{t_{2g}} \Gamma_i^3 (U_b^{(4)})$$

$$+ \sum_{i=1,2,3} \langle \Gamma_i^5 (u_a^{(4)}) \rangle_{t_{2g}} \Gamma_i^5 (U_b^{(4)})$$

$$= -(\tfrac{2}{21})^{1/2} a_4 \alpha_4 (\bar{l}_{za}^2 - \tfrac{2}{3}) \Gamma_1^3 (U_b^{(4)}) + \cdots , \quad \text{(B14)}$$

contribute to the anisotropic magnetoresistivity, Eq. (36). We evaluate α_4 by using Eqs. (B1) and (12) and $F^4 \cong 11\,600$ cm^{-1},[11] and find $\alpha_4 \cong 2550$ cm^{-1}; a_4 is given by Eq. (B3). By placing Eq. (B14) in Eq. (27a) and evaluating the anisotropy of the magnetoresistance as was done in Appendix A for the interaction H_2, we find that the anisotropy of the magnetoresistance for a polycrystalline sample is

$$\frac{\rho_\| - \rho_\perp}{\rho_0} = \frac{8}{7} (\tfrac{2}{21})^{1/2} \frac{a_4 \alpha_4}{\Delta_t} \frac{\sin^3 \eta_{2t} \cos \eta_{2t}}{\sin^2 \eta_0 + 3 \sin^2 \eta_{2t}}$$

$$\times \left(\sum_{\alpha' \alpha_3} [\delta_{\alpha' \alpha_3} - D_{\alpha' \alpha_3}^{(4)} (\tfrac{1}{2}\pi)] \rho_{\alpha_3}^{(2)} (\alpha') \right.$$

$$\left. - \sum_{\alpha' \alpha_5} [\delta_{\alpha' \alpha_5} - D_{\alpha' \alpha_5}^{(4)} (\tfrac{1}{2}\pi)] \rho_{\alpha_5}^{(2)} (\alpha') \right) ,$$

$$\text{(B15)}$$

where

$$\rho_{\alpha_i}^{(2)} (\alpha') \equiv \int (\tfrac{4}{5}\pi)^{1/2} Y_{2\alpha_i} (\hat{u}) \langle \Gamma_{\alpha'} (U_b^{(4)}) \rangle_{\vec{H}_\| \hat{u}} \, d\hat{u} ,$$

$$D_{\alpha' \alpha_i}^{(4)} = \sum_{mm'} \langle \alpha' | m' \rangle D_{m'm}^{(4)} (\tfrac{1}{2}\pi) \langle m | \alpha_i \rangle ,$$

and

$$a_4 \alpha_4 = -1625 \text{ cm}^{-1} .$$

The index α' runs over the partners of all the irreducible representations of the cubic group contained in the $3d$ rotation group representation $D^{(4)}$ [see Eq. (B4)], while α_3 runs over the two partners of Γ^3 and α_5 over the three partners of Γ^5.

We obtain an upper limit for the expression in large parentheses evaluating it for a single crystal with the current and a strong magnetic field parallel to a C_4 axis. Then in a strong field

$$\rho_{\alpha_i}^{(2)} (\alpha') = (\tfrac{4}{5}\pi)^{1/2} Y_{2\alpha_i} (0) \langle \Gamma_{\alpha'} (U_b^{(4)}) \rangle_{\vec{H} \| \hat{u}}$$

$$= \langle U_0^{(4)} \rangle_{\vec{H} \| \hat{u}} \langle 0 | \alpha' \rangle \langle \alpha_i | \alpha_{31} \rangle , \quad \text{(B16)}$$

and the expression reduces to

$$\left(\sum_m [\delta_{m0} - D_{0m}^{(4)} (\tfrac{1}{2}\pi, \phi)] \langle m | \alpha_{31} \rangle \right) \langle U_0^{(4)} \rangle_{\vec{H} \| \hat{u}} , \quad \text{(B16')}$$

where $\langle m | \alpha_{31} \rangle$ is given in Eq. (B5), i.e., $\langle 0 | \alpha_{31} \rangle = \sqrt{\tfrac{5}{12}}$ and $\langle \pm 4 | \alpha_{31} \rangle = -\sqrt{\tfrac{7}{24}}$. The matrix elements of the rotation $D_{0\pm4}^{(4)}$ introduce a spurious dependence (for a polycrystalline sample) in the angle that the field makes with respect to a c_4 axis perpendicular to the one along which the current points. We remove this dependence by averaging the expression over all angles ϕ. The expectation value $\langle U_0^4 \rangle$ evaluated for Ho^{3+} in a strong field is

$$\langle U_0^{(4)} \rangle = \langle 88 | U_0^{(4)} (L) | 88 \rangle$$

$$= \frac{\langle L = 6 \ S = 2 \ J = 8 \| U^{(4)} (L) \| L = 6 \ S = 2 \ J = 8 \rangle}{\langle J = 8 \| U_0^{(4)} (J) \| J = 8 \rangle}$$

$$\times \langle 88 | U_0^{(4)} (J) | 88 \rangle$$

$$= 17 \begin{Bmatrix} 8 & 8 & 4 \\ 6 & 6 & 2 \end{Bmatrix} \begin{pmatrix} 8 & 8 & 4 \\ 8 & -8 & 0 \end{pmatrix}$$

$$= 0.126 . \quad \text{(B17)}$$

By placing this value in Eq. (B16') and evaluating the rotation matrix elements we obtain

$$\sum_{\alpha'\alpha_3} [\delta_{\alpha'\alpha_3} - D^{(4)}_{\alpha'\alpha_3}(\tfrac{1}{2}\pi)]\rho^{(2)}_{\alpha_3}(\alpha')$$

$$- \sum_{\alpha'\alpha_5} [\delta_{\alpha'\alpha_5} - D^{(4)}_{\alpha'\alpha_5}(\tfrac{1}{2}\pi)]\rho^{(2)}_{\alpha_5}(\alpha') \lesssim 0.05. \quad (B18)$$

Upon placing this value in Eq. (B15) we find that the ratio of the contribution of the fourth-rank interaction H_4 to that of H_2, Eq. (35), is

$$\rho_a(H_4)/\rho_a(H_2) < -0.09. \quad (B19)$$

Thus the fourth-rank interaction makes a small contribution to the anisotropy of the magnetoresistance for Ho^{3+} impurities.

Finally, we consider the contribution of the octupolar interaction H_3, i.e., the spin-independent part of Eq. (4) with $k = 3$, to skew scattering. By using the values of the exchange integrals, Eq. (12), we find that for $4f^n$ electrons the interaction is

$$H_3 = -a_3\alpha_3 u^{(3)}_a \cdot U^{(3)}_b \text{ cm}^{-1}, \quad (B20)$$

where

$$a_3 \equiv \frac{(L\|\sum_{i=1}^{n} u^{(3)}_i \|L)}{(L\|U^{(3)}\|L)}$$

and

$$\alpha_3 = 8350 \text{ cm}^{-1}.$$

For example, for Ho^{3+}, $a_3 = -0.885$. From Appendix A we see that the only terms that contribute to the Hall resistivity are those proportional to Γ^4:

$$u^{(3)}_a \cdot U^{(3)}_b = \sum_{q=x,y,z} \Gamma^4_q(u^{(3)}_a) \Gamma^4_q(U^{(3)}_b) + \cdots, \quad (B21)$$

where, for example, $\Gamma^4_z(u^3) = u^3_0$, and the other terms can be found from Von der Lage and Bethe.[31]

The expectation values of $\Gamma^4_z(u^3)$ in the $5d$-t_{2g} states, Eq. (23), is

$$\langle u^{(3)}_0 \rangle_{t_{2g}} = -(\sqrt{\tfrac{2}{35}})\,\overline{m}, \quad (B22)$$

where $\overline{m} = 0, \pm 1$, while from the interaction H_1, Eq. (18), we found

$$\langle l_z \rangle_{t_{2g}} = -\overline{m}, \quad (B23)$$

Thus the interaction H_3 has a term which contributes to the Hall resistivity of the form

$$\langle H_3 \rangle_{t_{2g}} = (\sqrt{\tfrac{2}{35}})\,a_3\alpha_3 \sum_q \bar{l}_q \Gamma^4_q(U^{(3)}_b), \quad (B24)$$

where $\bar{l}_q$ is a component of the fictitious angular momentum with $\bar{l} = 1$.[29] Now, the contribution from H_1 was

$$\langle H_1 \rangle_{t_{2g}} = A_1 \vec{l} \cdot \vec{L}.$$

By using the same procedure as in Appendix A, we find that the term $\langle H_3 \rangle_{t_{2g}}$ makes the following contribution to the Hall angle, Eq. (41):

$$\phi(H_3) = \frac{6(\sqrt{\tfrac{2}{35}})a_3\alpha_3}{5\Delta_t} \frac{\sin^2\eta_{2t}\sin(2\eta_{2t}-\eta_1)\sin\eta_1}{\sin^2\eta_0 + 3\sin^2\eta_{2t}}$$

$$\times \sum_{m=0,\pm1} (\tfrac{4}{3}\pi)^{1/2} Y_{1\bar{m}}(\hat{H}) \langle \Gamma^4_{\bar{m}}(U^{(3)}) \rangle_{\vec{H}}, \quad (B25)$$

where the operators $\Gamma^4_{\bar{m}}(U^{(3)})$ are quantized along a c_4 axis of the local cubic-crystalline field.

In general, the expectation values $\langle \Gamma^4_{\bar{m}}(U^{(3)}) \rangle_{\vec{H}}$ do not vanish in a magnetic field. However, they do not have a term linear in H/T. This is readily established as follows, using $\Gamma^4_0(U^{(3)})$ as an example:

$$\langle U^{(3)}_0 \rangle = \text{Tr}(e^{-\beta H}U^{(3)}_0)/\text{Tr}\,e^{-\beta H}, \quad (B26)$$

where

$$H = V_{cr} + g_J\mu_B H J_z.$$

The term linear in H is

$$\frac{g_J\mu_B H}{kT} \frac{\text{Tr}(e^{-\beta V_{cr}} \int_0^1 dt\, e^{t\beta V_{cr}} J_z e^{-t\beta V_{cr}} U^{(3)}_0)}{\text{Tr}\,e^{-\beta V_{cr}}}. \quad (B27)$$

For high temperatures, i.e., those used in the experiments, $V_{cr}/kT \cong 0$, so that the trace in the numerator reduces to

$$p_3 \sum_{M_J=-J}^{J} \langle JM_J | J_z U^{(3)}_0(J) | JM_J \rangle. \quad (B28)$$

We have replaced $U^{(3)}_0(L)$ by $U^{(3)}_0(J)$ by using the relation

$$U^{(3)}_0(L) = p_3 U^{(3)}_0(J),$$

where

$$p_3 = \frac{(LSJ\|U^{(3)}(L)\|LSJ)}{(J\|U^{(3)}\|J)}. \quad (B29)$$

But the trace (B28) over the spherical basis vanishes because the operators J_z and $U^{(3)}_0(J)$ transform under different representations of the $3d$ rotational group, i.e.,

$$\langle J_z U^{(3)}_0(J) \rangle_{av} = 0. \quad (B30)$$

Therefore the interaction H_3 does not contribute to the term in the Hall resistivity, Eq. (44a), linear in H/T.

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