Theory of Indirect Exchange Interactions in Rare-Earth Metals

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Liu has recently considered the effect of nonzero atomic orbital angular momentum on the exchange interactions between a localized magnetic moment and conduction electrons. By expanding a part of the band wave functions in spherical harmonics, he found that the leading term gave rise to the familiar scalar product interaction between conduction electron spin and total atomic angular momentum J. In the present paper, we derive Liu's result by a simpler calculation, and obtain the first correction term in a similar expansion. Our main motivation in doing the latter is to investigate the validity of the common use of the leading term only, doubt being raised, *a priori*, by the fact that the Fermi wave vector times the radial extent of the $4f$ function is not $\ll 1$. We then investigate, in second-order perturbation theory, the magnetic interaction between atoms n and m. The leading term is, of course, an isotropic Heisenberg-type interaction $A_{nm}^{(0)} \mathbf{J}_n \cdot \mathbf{J}_m$ corresponding to Liu's result. The first correction term gives rise to anisotropic interactions including pseudo-dipolar forces and an unconventional interaction which is quartic in the J's. An estimate for rare-earth metals, based on free conduction electrons and screened hydrogenic localized functions, suggests that the comparative importance of the correction term is very sensitive to the number of $4f$ electrons and also to the lattice structure. For Tb through Er, it appears that the leading term does dominate, the correction being roughly 10%; for Tm metal the correction term is $\sim 30\%$, whereas for a single pair of Tm^{3+} ions it is $\approx 80\%$. The leading term is also considered using the same type of one-electron functions. This gives roughly the right order of magnitude for the Curie temperature and the correct signs for first- and second-neighbor interactions; also the ratio of the latter interactions is in rough agreement with experiment.

I. INTRODUCTION

THE indirect interaction between localized magnetic moments due to their exchange interactions with conduction electrons has been considered by many writers, including Zener,[1] Ruderman and Kittel,[2] Kasuya[3] and Yosida.[4] Most recently, Liu[5] investigated the effect of having an orbital contribution to the localized moment, as occurs in the rare-earth metals where **J**, the total orbital angular momentum of the $4f$ shell, is taken to be a good quantum number. Essentially expanding the conduction electron wave functions in spherical harmonics, Liu found the leading term in the band-localized exchange energy to be the familiar scalar product interaction between conduction electron spin and total atomic angular momentum **J**. This, of course, would lead in second-order perturbation theory, to the isotropic, Heisenberg-type of effective Hamiltonian. However, Liu's criterion for the validity of neglecting higher terms, namely, $k_F r_0 \ll 1$ ($k_F =$ Fermi wave vector, $r_0 =$ radial extent of the $4f$ orbital), is not very well satisfied, $k_F r_0$ being roughly 0.5, leading one to suspect that higher terms might not be much smaller than the leading term. In view of this and the importance recently attached to anisotropy energy in

determining the magnetic ordering found in the heavy rare-earth metals,[6–9] it is of interest to estimate the higher terms (these terms, as far as we know, have never been looked at, and would be expected to lead to anisotropic coupling quite analogously to the "pseudo-anisotropics" first discussed by Van Vleck[10] in connection with iron group atoms).

In the present paper, we first derive Liu's result by a simpler and more direct technique. We then use this technique and an approximation procedure similar to Liu's, plus second-order perturbation theory (following previous authors[2–4]) to calculate the indirect exchange forces. Order-of-magnitude estimates are made using the free-electron model for the band electrons, and screened hydrogenic localized functions.

In the lowest order approximation we find the expected isotropic interactions, $-\sum A_{nm}^{(0)} \mathbf{J}_n \cdot \mathbf{J}_m$. The first correction term H_2 involves a contribution to the isotropic forces as well as anisotropic energies. The latter include single-particle and two-particle forces which are quadratic in the **J**'s (the two-particle forces may properly be called pseudodipolar interactions) and terms, quartic in the **J**'s, which are of unconventional form. The results show that the relative importance of

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[2] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954), referred to hereafter as R-K.

[3] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).

[4] K. Yosida, Phys. Rev. **106**, 893 (1957).

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[7] T. A. Kaplan, Phys. Rev. **124**, 329 (1961).

[8] R. J. Elliott, Phys. Rev. **124**, 346 (1961).

[9] H. Miwa and K. Yosida, Progr. Theoret. Phys. (Kyoto) **26**, 693 (1961).

[10] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

the correction term compared to the zero-order term is very sensitive both to the number of $4f$ electrons and the lattice structure. For the simplest theoretical model, in which there is a single hole in the $4f$ shell (i.e., Yb^{3+}, which doesn't occur in the metal), H_2 is larger than H_0 for a single pair of Yb^{3+} ions in the conduction electron sea and is of the same order as H_0 for a hcp lattice of ions. For a single pair of Tm^{3+} ions $H_2 \sim 80\%$, whereas for Tm metal it is about 30%; for Er, Ho, Dy, and Tb the leading term dominates, the correction being roughly 10%.[11]

One result somewhat incidental to our general objectives has appeared in our present investigation. We found $A_{nm}^{(0)}$ to be expressed as the same integral found previously[4] to lead to the well-known Ruderman-Kittel formula. However, a more careful evaluation of this integral leads to a modification, significant for the rare earths, of the R-K formula.

Some aspects of the bearing of our results on the magnetic ordering problem in the rare earths are also discussed.

II. THE EXCHANGE HAMILTONIAN

The physical picture that is taken to describe the low-lying zero-order states of the metal is as follows: There are, in every such state, n localized electrons at each atomic site, and hence a fixed number of conduction electrons. The localized "orbitals" are Russell-Saunders functions $\psi_{LSJM}^{(a)}(1,\cdots,n)$, where L, S, and J are, respectively, the orbital, spin, and total angular momentum quantum numbers, $M = -J, \cdots, J$, and a, which identifies the site, runs from 1 to N, the total number of atoms. Since L and S are constant, they may be dropped. The band orbitals are products of Bloch functions, $\phi_k = \exp(i\mathbf{k}\cdot\mathbf{r})u_k(\mathbf{r})$, and spin functions α_σ ($\sigma = \pm\frac{1}{2}$). The orbital $\psi_{JM}^{(a)}$ is an antisymmetrized linear combination of products of equivalent atomic one-electron functions $\chi_{\lambda\mu}\alpha_\sigma$ where λ, μ, and σ are the orbital and spin angular momentum quantum numbers; e.g., the $\chi_{\lambda\mu}$ would be $4f$ atomic functions for the rare-earth problem. Furthermore, all the one-electron functions (including the band functions) are assumed to be mutually orthogonal.

The matrix elements corresponding to indirect exchange are then

$$(M', a, \mathbf{k}'\sigma' | V | M, a, \mathbf{k}\sigma)$$

$$= -n\left(\psi_{JM'}^{(a)}(1\cdots n)\phi_{\mathbf{k}'\sigma'}(n+1), \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_{n+1}|}P_{1,n+1}\right.$$

$$\left. \times \psi_{JM}^{(a)}(1\cdots n)\phi_{\mathbf{k}\sigma}(n+1)\right)$$

$$\equiv V^{(a)}(M', M; \mathbf{k}'\sigma', \mathbf{k}\sigma), \quad M \neq M'$$

$$(M, a, \mathbf{k}'\sigma' | V | M, a, \mathbf{k}, \sigma) = \sum_{b=1}^{N} V^{(b)}(M, M; \mathbf{k}'\sigma', \mathbf{k}\sigma). \quad (1)$$

The notation $(M', a, \mathbf{k}'\sigma' | \cdot | M, a, \mathbf{k}, \sigma)$ means that the final state is obtained from the initial by replacing $\phi_{\mathbf{k}\sigma} = \phi_{\mathbf{k}}\alpha_0$ by $\phi_{\mathbf{k}'\sigma'}$, and changing the state corresponding to site a from M to M', with J fixed (the constancy of J, which is discussed below, is not a needed restriction at this point). P_{ij} permutes coordinates (spin and space) i and j. We have used the fact that $\psi_{JM}^{(a)}(1\cdots n)$ is antisymmetrized; the full crystal state is also anti-symmetric, of course. The first of (1) was used by Liu,[5] but the second differs in that we have removed his restriction to a single atomic site. These two formulas may be conveniently summarized by introducing the replacement operators $A_{\mathbf{k}'\sigma',\mathbf{k}\sigma}$ (replaces $\phi_{\mathbf{k}\sigma}$ by $\phi_{\mathbf{k}'\sigma'}$) and $A_{M',M}^{(a)}$ [replaces $\psi_{JM}^{(a)}$ by $\psi_{JM'}^{(a)}$]; letting C_{ij} stand for either of these, $C_{ij} = 0$ if orbital j is not present in ψ.[12] Then the operator

$$W = \sum_{\mathbf{k},\sigma,\mathbf{k}',\sigma'} \sum_{b,M,M'} V^{(b)}(M', M; \mathbf{k}'\sigma', \mathbf{k}\sigma)A_{\mathbf{k}'\sigma',\mathbf{k}\sigma}A_{M'M}^{(b)}$$

evidently gives the matrix elements (1). This reduces to Kasuya's expression[3] for the case of one localized s electron per site. It is convenient to use the properties of the Bloch functions to rewrite W as

$$W = \sum_{\mathbf{k},\sigma,\mathbf{k}'\sigma'} \sum_{b,M,M'} \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_b]$$

$$\times V(M', M; \mathbf{k}'\sigma', \mathbf{k}\sigma)A_{\mathbf{k}'\sigma',\mathbf{k}\sigma}A_{M'M}^{(b)}, \quad (2)$$

where V is obtained from $V^{(b)}$ by replacing the localized functions $\psi_{JM}^{(b)}$ centered at $\mathbf{R}_b$ with the one, ψ_{JM}, centered at $\mathbf{R} = 0$.

One could now express $A_{M'M}^{(b)}$ as an explicit function of $\mathbf{J}_b$, the total angular momentum operator for site b, analogously to Kasuya's replacing $A_{M'M}^{(b)}$ by a function of $\mathbf{S}_b$ for his s-state example. However, we shall instead essentially follow Liu and write

$$\psi_{JM}(1\cdots n) = \sum_{\mu\sigma} F_{\mu\sigma}^{JM}(2\cdots n)\chi_{l\mu}(\mathbf{r}_1)\alpha_\sigma(1); \quad (3)$$

[this is like Liu's expansion of his $\psi_{Lm}(\mathbf{r}_1\cdots\mathbf{r}_n)$ for the case of a less-than-half-filled shell]. Then

$$V(M', M; \mathbf{k}'\sigma', \mathbf{k}\sigma)$$

$$= -n \sum_{\mu\mu',ss'} (F_{\mu's'}^{JM'}, F_{\mu s}^{JM})I_{\mu'\mu}(\mathbf{k}',\mathbf{k})$$

$$\times (\alpha_{s'}(1)\alpha_{\sigma'}(2), P_{12}^\sigma\alpha_s(1)\alpha_\sigma(2)), \quad (4)$$

where

$$I_{\mu'\mu}(\mathbf{k}',\mathbf{k}) = \left(\chi_{\lambda\mu'}(\mathbf{r}_1)\phi_{\mathbf{k}'}(\mathbf{r}_2), \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}P_{12}^r\chi_{\lambda\mu}(\mathbf{r}_1)\phi_k(\mathbf{r}_2)\right).$$

$$(5)$$

P_{ij}^r permutes space variables $\mathbf{r}_i$ and $\mathbf{r}_j$, and P_{ij}^σ permutes spin function arguments.

We may also expand the space part of the band

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[11] It will be recalled that a value of 10% was found for the anisotropy in Dy by S. H. Liu, D. R. Behrendt, S. Legvold, and R. H. Good, Jr., Phys. Rev. 116, 1464 (1959).

[12] $A_{\mathbf{k}'\sigma',\mathbf{k}\sigma}$ is just the product $a_{\mathbf{k}'\sigma'}^\dagger a_{\mathbf{k}\sigma}$ of fermion creation and destruction operators, as is $A_{M'M}^{(a)}$ for the case of one localized electron.

function in spherical harmonics,[13]

$$\phi_k(\mathbf{r}) = \sum_{lM} B_{lM}(\mathbf{k},r) Y_{lM}(\mathbf{r}), \qquad (6)$$

and similarly expand $|\mathbf{r}_1 - \mathbf{r}_{n+1}|^{-1}$; when only the term $l = M = 0$ in (6) contributes, we obtain

$$V(M',M; \mathbf{k}'\sigma',\mathbf{k}\sigma)$$

$$= -n\mathcal{J}(\mathbf{k}',\mathbf{k}) \sum_{\mu\mu',ss'} (F_{\mu's'}{}^{JM'},F_{\mu s}{}^{JM})(\chi_{\lambda\mu'},\chi_{\lambda\mu})$$

$$\times (\alpha_{s'}(1)\alpha_{\sigma'}(n+1), P_{1,n+1}{}^{\sigma}\alpha_s(1)\alpha_\sigma(n+1)), \quad (7)$$

where

$$\mathcal{J}(\mathbf{k}',\mathbf{k}) = \frac{e^2}{2\lambda+1} \int dr_1 dr_2\, r_1{}^2 r_2{}^2 \frac{r_<{}^\lambda}{r_>{}^{\lambda+1}} R_\lambda(r_1) R_\lambda(r_2)$$

$$\times B_{00}(\mathbf{k}',r_2)^* B_{00}(\mathbf{k},r_1),$$

where R_λ is the radial part of $\chi_{\lambda\mu}$. It immediately follows that

$$V(M',M; \mathbf{k}'\sigma',\mathbf{k}\sigma) = -n\mathcal{J}(\mathbf{k}',\mathbf{k})(\psi_{JM'}(1\cdots n)\alpha_{\sigma'}(n+1)),$$

$$\times (\tfrac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_{n+1}) \psi_{JM}(1\cdots n)\alpha_\sigma(n+1), \quad (8)$$

which becomes identical to Liu's result (19) when the band functions are specialized as he did. Note that $n\mathbf{s}_1$ may be replaced here by $\mathbf{S}$, the total atomic spin. (We used Dirac's[14] well-known identity for the permutation of spins.)[15]

The complete expansion (6) gives

$$V(M',M; \mathbf{k}'\sigma',\mathbf{k}\sigma)$$

$$= -n \sum_{l'L} \sum_{\mu s} \sum_{\mu' s'} \sum_{mm'} (F_{\mu's'}{}^{JM'},F_{\mu s}{}^{JM})$$

$$\times \mathcal{J}(\mathbf{k}',\mathbf{k}; l'm',lmL)(Y_{\lambda\mu'},Q(lm,l'm',L)Y_{\lambda\mu})$$

$$\times (\alpha_{s'}(1)\alpha_{\sigma'}(2), P_{12}{}^\sigma \alpha_s(1)\alpha_\sigma(2)),$$

where

$$\mathcal{J}(\mathbf{k}',\mathbf{k}; l'm',lm,L)$$

$$= \frac{e^2}{2L+1} \int dr_1 dr_2\, R(r_1) R(r_2) B_{l'm'}{}^*(\mathbf{k}',r_2)$$

$$\times B_{lm}(\mathbf{k},r_1) \frac{r_<{}^L}{r_>{}^{L+1}} r_1{}^2 r_2{}^2, \quad (9)$$

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[13] The Y_{lm} are normalized and have phases defined as in M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

[14] P. A. M. Dirac, *Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1947), 3rd ed.

[15] The relative simplicity of the present derivation lies in the fact that it was not necessary here to explicitly write the ψ_{JM} in terms of the Clebsch-Gordan coefficients and the ψ_{Lm}, thereby avoiding the complications of having to treat the cases of less-than- and more-than-half-filled shells separately, to consider Young diagrams, etc. This simplification was obtained by using the expansion of Eq. (3) for the atomic wave function instead of Liu's similar expansion for the spatial part only.

and $Q(\ )$ are the one-electron operators defined by

$$4\pi \sum_M (Y_{\lambda\mu'}, Y_{LM} Y_{lm})(Y_{l'm'}, Y_{LM}^* Y_{\lambda\mu})$$

$$= (Y_{\lambda\mu'}, Q(lm,l'm',L) Y_{\lambda\mu}). \quad (10)$$

For a given value of $lm \cdots L$, Q can be written explicitly as a linear combination of Y_{pq} or, alternately, as a function of the single-particle orbital angular momentum operators $\mathbf{l}$. For example, $Q(00,00,L) = \delta_{\lambda L}$, the operators that entered into (7); other examples will be given below. We can perform the sum over $\mu s\mu's'$ to give the result

$$V(M',M; \mathbf{k}'\sigma',\mathbf{k}\sigma)$$

$$= -n \sum_{ll'} \sum_{Lmm'} \mathcal{J}(\mathbf{k}',\mathbf{k}; l'm',lm,L)$$

$$\times \langle JM'\sigma' | Q_1(lm,l'm',L) P_{1,n+1}{}^\sigma | JM\sigma \rangle$$

$$= \sum_{ll'} V(ll'); \quad (11)$$

the subscript on Q means that Q operates on particle 1 and $|JM\sigma\rangle$ means $\psi_{JM}(1\cdots n)\alpha_\sigma(n+1)$.

Calling the terms in (11) with $l+l'=p$ the pth term in the series (11), we see that the 0th term is just (7) (which contains Liu's result). As discussed by Liu, the convergence of this series is rapid if the band electrons are essentially free, and $k_F r_0 \ll 1$ where k_F is the Fermi wave vector and r_0 is the radial extent of the localized orbitals.[16] However, in the rare-earth metals $k_F r_0$ is not very small (it is around $\tfrac{1}{2}$), leading one to question the assumption that the leading term is dominant.

Some light is thrown on this question by calculating the first correction term on the basis of free-electron band functions, namely,

$$\phi_k(\mathbf{r}) = \Omega^{-1/2} \exp(i\mathbf{k}\cdot\mathbf{r}), \quad (12)$$

where Ω is the volume of the crystal. Then

$$\mathcal{J}(\mathbf{k}',\mathbf{k}; l'm',lm,L) = \frac{(4\pi e)^2}{\Omega(2L+1)} i^{l-l'} Y_{l'm'}(\hat{k}')$$

$$\times Y_{lm}(\hat{k}) \mathcal{J}(k'k,l'lL), \quad (13)$$

where

$$\mathcal{J}(k'k,l'lL) = \int dr_1 dr_2\, R(r_1) R(r_2)$$

$$\times j_{l'}(k'r_2) j_l(kr_1) \frac{r_<{}^L}{r_>{}^{L+1}} r_1{}^2 r_2{}^2, \quad (14)$$

and $j_l(x)$ are the spherical Bessel functions. Following

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[16] A probably important modification of $\exp(i\mathbf{k}\cdot\mathbf{r})$ for the band functions, namely, orthogonalization to the core electrons, will not affect the convergence properties. This follows from the consideration that the only appreciable contribution to (9) from the core functions mixed into ϕ_k will come from those core functions associated with the atom at $R=0$. Hence, as far as (9) is affected, the $C_{\lambda m}$ in (4) will be changed only for the (finite) number of λ values present in the core. On the other hand, if other plane waves $\exp[i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}]$ with $|\mathbf{k}_F + \mathbf{K}| r_0 > 1$ are added the rate of convergence might be altered.

Kasuya's remark that the exchange integral is essentially a function only of the momentum transfer $\mathbf{k}-\mathbf{k}'$, we make an approximation that simplifies things considerably. In (13) and (14) we put $\mathbf{k}=\mathbf{k}'+\mathbf{q}$ and then put $k'=0$, which gives (5) as a function of $\mathbf{q}$ only.[17] Then,

$$\mathfrak{g}(k'k,l'lL)=\mathfrak{g}(0q,l'lL)=\mathfrak{g}(qlL)\delta_{l'0} \qquad (15)$$

since $j_{l'}(0)=\delta_{l'0}$. Then the double sum (11) reduces to the single sum

$$V(M',M\,;\,\mathbf{k}'\sigma',\mathbf{k}\sigma)=\sum_l V(l), \qquad (16)$$

where

$$V(l)=-n\sum_{Lm}\mathfrak{g}(0,\mathbf{q}\,;\,00,m,L)$$

$$\times\langle JM'\sigma'|Q_1(lm,00,L)P_{1,n+1}{}^\sigma|JM\sigma\rangle$$

$$=-n\sum_m\mathfrak{g}(0,\mathbf{q}\,;\,00,m,\lambda)$$

$$\times\langle JM'\sigma'|Q_1(lm,00,\lambda)P_{1,n+1}{}^\sigma|JM\sigma\rangle \qquad (17)$$

since $Q_1(lm,00,L)=0$ unless $L=\lambda$. From (10),

$$(Y_{\lambda\mu'}Q(lm,00,\lambda)Y_{\lambda\mu})=(4\pi)^{1/2}\int Y_{\lambda\mu'}{}^*Y_{lm}Y_{\lambda\mu}d\Omega \qquad (18)$$

so that, as far as these matrix elements are concerned, $Q(lm,00,\lambda)$ is just $(4\pi)^{1/2}$ times the spherical harmonic operator Y_{lm}. Note that this is zero unless l is even. Equations (16), (17), and (18) with the previous definitions give the approximate evaluation of the exchange matrix element $V(M',M\,;\,k'\sigma'k\sigma)$ that is used in the next section to investigate the indirect exchange interaction between two localized moments.

III. THE EFFECTIVE HAMILTONIAN

The effective exchange Hamiltonian[18] corresponding to (2) [which operates in the space of the $(2J+1)^N$ functions, each defined as having one atomic orbital per site, $\psi_{JM}{}^{(b)}$, occupied and free electron band states occupied to the Fermi surface] is given in second-order perturbation theory by[19]

$$\langle\alpha|\tilde{H}_{\text{ex}}|\beta\rangle=\sum_{b,b'}\sum_{k\sigma k'\sigma'}\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_{b'}-\mathbf{R}_b)]}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}$$

$$\times V(M_b{}^\alpha M_b{}^\beta\mathbf{k}'\sigma'\mathbf{k}\sigma)V(M_{b'}{}^\alpha M_{b'}{}^\beta\mathbf{k}\sigma\mathbf{k}'\sigma'), \qquad (19)$$

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[17] Because of the factor $1/r_{12}$ in (5), most of the integral will come from r_1 or r_2. Hence, we may put $\phi_k{}'^*(\mathbf{r}_2)\phi_k(\mathbf{r}_1)$ $=\Omega^{-1}\exp[i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)]\exp(i\mathbf{q}\cdot\mathbf{r}_1)\cong\Omega^{-1}\exp(i\mathbf{q}\cdot\mathbf{r}_1)$. This approximation is justified in Appendix 1 in somewhat more detail.

[18] See for example, P. Löwdin, J. Chem. Phys. 19, 1396 (1951).

[19] First-order perturbation theory is included in this when limit $N\rightarrow\infty$ is taken, as shown previously (references 3, 4). We also follow these authors in neglecting the difference between the distributions of "spin-up" and "spin-down" conduction electrons in the unperturbed states.

with $\epsilon(\mathbf{k})=\hbar^2k^2/2m$, as is easily seen by using (2). Here $M_b{}^\alpha$ is the M number at site b in state α, etc., and the summations over $\mathbf{k}$ and $\mathbf{k}'$ are restricted, respectively, to outside and inside the Fermi sphere. The intermediate states that were considered in obtaining (19) are those in which a band electron is excited, and the M's change, the J's being fixed.[20] Using (11) and performing the sum over σ,σ', this becomes

$$\tilde{H}_{\text{ex}}=n^2\sum_{bb'}\sum_{kk'}\sum_{lml'm'}\sum_{pnp'n'}\sum_{LL'}\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{bb'}]}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}$$

$$\times\mathfrak{g}(\mathbf{k}',\mathbf{k}\,;\,l'm'lmL)\mathfrak{g}(\mathbf{k},\mathbf{k}'p'n'pnL')$$

$$\times Q_1{}^b(lml'm'L)Q_1{}^{b'}(pnp'n'L')(\tfrac{1}{2}+2\mathbf{s}_1{}^b\cdot\mathbf{s}_1{}^{b'}), \qquad (20)$$

where $Q_1{}^b$ operates on the coordinates of an electron at site b (i.e., in $\psi_{JM}{}^{(b)}$). Thus, Eq. (20) expresses the indirect exchange interaction, exact to second order, in terms of single-electron spin and orbital angular momentum [as per the discussion following Eq. (10)].

To get an idea as to the physical meaning of (20), we first use the approximation at the end of the previous section, simplifying (20) to

$$\tilde{H}_{\text{ex}}=4\pi n^2\sum_{bb'}\sum_{kk'}\sum_{lm}\sum_{pn}\frac{\exp(i\mathbf{q}\cdot\mathbf{R}_{bb'})}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}\mathfrak{g}(\mathbf{q}\,;\,lm\lambda)\mathfrak{g}^*(\mathbf{q}\,;\,pn\lambda)$$

$$\times Y_{lm}{}^b Y_{pn}{}^{b'*}(\tfrac{1}{2}+\mathbf{s}_1{}^b\cdot\mathbf{s}_1{}^{b'}), \qquad (21)$$

where we have used (18),

$$\mathfrak{g}(\mathbf{q}\,;\,lm\lambda)=\mathfrak{g}(0,\mathbf{q}\,;\,00,m\lambda)$$

$$=\frac{(4\pi e)^2}{(4\pi)^{\frac{1}{2}}\Omega(2\lambda+1)}i^l Y_{lm}{}^*(\hat{q})\mathfrak{g}(q,l\lambda), \qquad (22)$$

$$\mathfrak{g}(ql\lambda)=\int dr_1 dr_2\,R(r_1)R(r_2)j_l(qr_1)$$

$$\times(r_<{}^\lambda/r_>{}^{\lambda+1})r_1{}^2 r_2{}^2. \qquad (23)$$

We note that the operators that appear in the approximate expression (21) all appear in the exact Eq. (20), but some in the latter have zero coefficients in (21), e.g., Q's for $l=l'=1$. In other words, the type of operators that we discuss (21) appear in a rigorous

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[20] As pointed out by Brout and Suhl [Phys. Rev. Letters 2, 387 (1959)], the intermediate states include states with atomic angular momentum $J'\neq J$, the value in the lowest multiplet. However, their formula for the contribution to the isotropic Heisenberg-type coupling between atoms b and b' arising from such excitations is incorrect. In fact, these excitations contribute nothing to such interactions in second-order perturbation theory, since only one atom can have $J'\neq J$ in any virtual state (by definition, at least one conduction electron is excited). Hence, there can be no interaction between different sites b and b' arising from these terms. Such excitations do give rise to single-atom indirect-exchange anisotropy forces only when the energy bands are not spherically symmetric [so they are omitted in (19)], and these forces will be small in the rare earths (with the possible exception of Eu and Sm).

theory; the operators omitted have small coefficients if (12) is not a bad approximation.

Putting $\mathbf{k}=\mathbf{k}'+\mathbf{q}$ in the usual way, and carrying out the $\mathbf{k}'$ integration and the integration over the directions of $\mathbf{q}$, (21) becomes

$$\tilde{H}=-\left(\frac{2ne^2}{2\lambda+1}\right)^2\frac{mk_F}{\pi\hbar^2}\sum_{bb'}\sum_{lpm}X(R_{bb'},lpm)$$

$$\times Y_{lm}{}^b Y_{p,-m}{}^{b'}(\tfrac{1}{2}+2\mathbf{s}_1{}^b\cdot\mathbf{s}_1{}^{b'}),\quad(24)$$

where

$$X(R_{bb'},lpm)=\sum_{L=0}^{\infty}K(R_{bb'},lpL)i^L(2l+1)(2p+1)$$

$$\times C(lpL;-m,m)C(lpL;00),\quad(25)$$

$$K(R,lpL)=i^{l-p}\int_0^{\infty}dq\,q^2 f(q/2k_F)$$

$$\times\mathcal{G}(ql\lambda)\mathcal{G}(qp\lambda)j_L(qR),\quad(26)$$

$$f(x)=1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|,\quad(27)$$

and the $C(\cdots)$ are the Clebsch-Gordan coefficients in Rose's notation.[18] The latter arose from the integral over $\hat{q}$ which involved products of three $Y(\hat{q})$'s.[18] These came about after expanding $\exp(i\mathbf{q}\cdot\mathbf{R}_{bb'})$ in spherical harmonics with arguments referred to a coordinate system with the z axis along $R_{bb'}$. This choice of z axis uniquely defines the $Y_{lm}{}^b$ in (24) for each term $(bb'$ pair) in the sum; note that, although the notation is not explicit, this definition varies from pair to pair.

For the case considered previously[3,4] of one localized s electron, $n=1$, $\lambda=0$, and only $l=p=L=m=0$ contributes, (24) reducing to the proper expression.[3,4] $[\mathcal{G}(q00)$ is just $1/4\pi$ times Yosida's $I(q)$.] For the general case, the leading term in (24) is the one for $l=p=0$, the first correction term coming from $(lp)=(02)$ and (20). The integral $K(R,000)$ was previously evaluated[4] by putting $\mathcal{G}(q00)\sim\mathcal{G}(000)$, leading to the Ruderman-Kittel function.[2] However, such an approximation is entirely inadequate for our purposes, since $\mathcal{G}(0l\lambda)=0$ for $l>0$, so that all the correction terms would vanish. Hence, we must look at the integral (26) more carefully. Putting $K(R,n0n)=K_n(R)$, and $\mathcal{G}(q0\lambda)\mathcal{G}(qn\lambda)=\gamma_n(q)$ for $n=0,2$, it is found in Appendix 2 that

$$K_n(R)=\frac{\pi\gamma_n(q_0)}{R^3}\Bigg[-\cos q_0 R$$

$$+(a_n+b_n)\frac{\sin q_0 R}{q_0 R}+O(q_0{}^{-2}R^{-2})\Bigg],\quad(28)$$

where

$$a_0=1,\quad a_2=4,$$

$$b_n=2q_0\gamma_n{}'(q_0)/\gamma_n(q_0).\quad(29)$$

Since $q_0 R\sim10$ for nearest neighbor R, (28) is rapidly convergent for reasonable functions $\gamma(q)$.

If $\gamma_0(q)$ were constant, (28) would be exact with $b_0=0$, and $O(q_0{}^{-2}R^{-2})\equiv0$, so that K_0 would be $\pi\gamma_0 q_0{}^3$ times the Ruderman-Kittel function

$$F(q_0 R)=\frac{1}{(q_0 R)^3}\left(\frac{\sin q_0 R}{q_0 R}-\cos q_0 R\right).$$

Hence, for the leading term $(n=0)$, our result (28) differs from Yosida's[4] both in the shape of the function of R (since $b_0\neq0$) and in the value of the over-all coefficient [Yosida's formula replaces $\gamma(q_0)$ by $\gamma(0)$]. We shall see that neither of these differences are negligible. It should be pointed out that our evaluation of this integral is of interest whenever one makes the common assumption $\mathscr{s}(\mathbf{k},\mathbf{k}',\cdots)\cong$a function of $\mathbf{k}-\mathbf{k}'$, and $\epsilon(\mathbf{k})\propto k^2$, i.e., it goes beyond our simple model for the band functions.

To conclude this section we write explicitly the leading term $(l=p=0)$ and the first correction terms, $(lp)=(20)$ and (02), in (24). These are quite simple since $C(00L;-m,m)=\delta_{L0}\delta_{m0}$, $C(02L;-m,m)=\delta_{L2}$, and only $m=0$ contributes to the "02" term because of the Y operators. Hence, we get

$$\tilde{H}=H_0+H_2+\cdots,\quad(30)$$

where

$$H_0=-G\sum_{ab}K(R_{ab})(\tfrac{1}{2}+2\alpha_J{}^2\mathbf{J}_a\cdot\mathbf{J}_b),\quad(31)$$

$$H_2=(20\pi)^{\frac{1}{2}}n^2G\sum_{ab}K_2(R_{ab})(\tfrac{1}{2}+2\mathbf{s}_1{}^a\cdot\mathbf{s}_1{}^b)(Y_{20}{}^a+Y_{20}{}^b)$$

$$=\frac{5n^2G}{(2\lambda+3)(2\lambda-1)}\sum_{ab}K_2(R_{ab})(\tfrac{1}{2}+2s_1{}^a\cdot s_1{}^b)$$

$$\times[2\lambda(\lambda+1)-3(\hat{R}_{ab}\cdot\mathbf{l}_{1a})^2-3(\hat{R}_{ab}\cdot\mathbf{l}_{1b})^2],$$

$$G=\frac{e^4}{\pi^2(2\lambda+1)^2}\frac{mk_F}{\hbar^2},\quad(32)$$

and α_J+1 is the Landé g factor. We have used the well-known fact that matrix elements of $n\mathbf{s}_1{}^b$ between states of given J are the same as those of $\alpha_J\mathbf{J}_b$, and also

$$Y_{20}\equiv\left(\frac{5}{4\pi}\right)^{\frac{1}{2}}\frac{\lambda(\lambda+1)-3l_z{}^2}{(2\lambda+3)(2\lambda-1)},$$

as can be seen by doing the integral in (18). Here, l_z is the z component of the single-particle orbital angular momentum operator $\mathbf{l}$, and the argument θ of Y_{20} is measured from the z axis; this is why the component along $\mathbf{R}_{ab}$ enters in (32). The expression of (32) as a function of the total atomic orbital angular momenta $\mathbf{J}_a$, which is much more convenient for the discussion of magnetic ordering, depends on the details of the

n-particle atomic function. In the next section this is done for the simplest cases of one electron and one hole in the $4f$ shell; in Appendix 4 the calculation for arbitrary n is carried out.

IV. $\tilde{H}_{ex}$ AS A FUNCTION OF THE J_a; ESTIMATE OF TERMS FOR RARE EARTHS

Writing

$$H_2 = \frac{5G}{(2\lambda+3)(2\lambda-1)} \sum_{ab} K_2(R_{ab})\Gamma_{ab}, \quad (33)$$

we have

$$\Gamma_{ab} = 2\lambda(\lambda+1)(\tfrac{1}{2}n^2 + 2\alpha_J{}^2 \mathbf{J}_a \cdot \mathbf{J}_b) - \frac{3n}{2}\sum_{i=1}^{n}(l_{iaz}{}^2 + l_{ibz}{}^2)$$

$$- 6(\mathbf{S}_a \cdot \sum_i s_{ib} l_{ibz}{}^2 + \mathbf{S}_b \cdot \sum_i s_{ia} l_{iaz}{}^2), \quad (34)$$

where $\mathbf{S}_a = \sum_i \mathbf{s}_{ia}$ (the total atomic spin for a site a); advantage has been taken of the antisymmetry of the basis functions $\psi_{JM}{}^a$; for given ab, $\mathbf{R}_{ab}$ is the z axis, as we have said.

We first consider the special cases of a half-filled atomic shell, one atomic electron and one hole. The half-filled shell case is trivial in our approximation (30), since the series terminates at the first term.[21] For one electron, obviously,

$$\Gamma_{ab}{}^{(el)} = 2\lambda(\lambda+1)(\tfrac{1}{2} + 2\alpha_J{}^2 \mathbf{j}_a \cdot \mathbf{j}_b) - \tfrac{3}{2}(l_{az}{}^2 + l_{bz}{}^2)$$

$$- 6\mathbf{s}_a \cdot \mathbf{s}_b(l_{az}{}^2 + l_{bz}{}^2), \quad (35)$$

lower case letters having been used to emphasize that these are one-particle operators (even though for this case they also are "total" operators). For the case of one hole, we relate the operators $\sum_{i=1}^{n} l_{iaz}{}^2$, etc., to operators that operate on one-particle wave functions by means of the usual correspondence.[22] This gives

$$\Gamma_{ab}{}^{(hole)} = 2\lambda(\lambda+1)(\tfrac{1}{2}n^2 + 2\alpha_J{}^2 \mathbf{j}_a \cdot \mathbf{j}_b)$$

$$- \tfrac{3}{2}n[\tfrac{2}{3}\lambda(\lambda+1)(2\lambda+1) - l_{az}{}^2 - l_{bz}{}^2] -$$

$$6\mathbf{s}_a \cdot \mathbf{s}_b[l_{az}{}^2 + l_{bz}{}^2]. \quad (36)$$

Aside from constant terms (and the fact that, for the ground term, $J = \lambda \pm 1/2$, $-$ for electron, $+$ for hole) the only change from one electron to one hole is the factor of $-n$ in the term $(l_{az}{}^2 + l_{bz}{}^2)$. (Remember that n is the total number of *electrons*.)

To finally express the operators completely in terms of the $\mathbf{j}_a$, $\mathbf{j}_b$, use is made of the explicit form of the wave functions ψ_{JM} for one particle. By direct calculation one finds, for example, that

$$(\psi_{JM'}, s_+ l_z{}^2 \psi_{JM}) = \tfrac{1}{2}\alpha_J(\psi_{JM'}, j_+ (j_z + \tfrac{1}{2})^2 \psi_{JM}).$$

Proceeding in this way, one obtains after a little

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[21] This is not true in the general case, Eq. (20). See Appendix 1 for discussion of the latter.

[22] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1951).

TABLE I. Atomic parameters P_i.

	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+} a
P_1	0	0.606	0.964	0.667	-1.31	-8.18	-38
P_2	0	0.167	0.154	0.0714	-0.103	-0.500	-2
P_3	0	-1.10	-1.24	-0.610	0.824	3.27	8.17

a This case, Yb^{3+}, does not exist in the metal.

manipulation, the result

$$H_2 = \frac{5G}{(2\lambda+3)(2\lambda-1)} \sum_{ab} K_2(R_{ab})$$

$$\times \{ C_1[(\hat{R}_{ab} \cdot \mathbf{J}_a)^2 - \tfrac{1}{3}J(J+1)] + C_2[(\hat{R}_{ab} \cdot \mathbf{J}_a)(\hat{R}_{ab} \cdot \mathbf{J}_b)$$

$$- \tfrac{1}{3}\mathbf{J}_a \cdot \mathbf{J}_b] - C_3[(\hat{R}_{ab} \cdot \mathbf{J}_a)^2 \mathbf{J}_a \cdot \mathbf{J}_b + \mathbf{J}_a \cdot \mathbf{J}_b(\hat{R}_{ab} \cdot \mathbf{J}_a)^2$$

$$- \tfrac{2}{3}J(J+1)\mathbf{J}_a \cdot \mathbf{J}_b] \} \quad (43)$$

where for one hole and for one electron,

$$C_1 = 3n(1-2\alpha_J), \text{ one hole}$$

$$= -3(1-2\alpha_J), \text{ one electron,}$$

$$C_2 = 6\alpha_J(1-\alpha_J), \quad (43a)$$

$$C_3 = 6\alpha_J{}^2.$$

A simple check on (43) is obtained by considering one s electron, so that $\alpha_J = 1$, $J_{az}{}^2 = 1/4$; (43) then vanishes as it should.

We see that the first correction term H_2 contains, in addition to a contribution to the isotropic interaction $\mathbf{J}_a \cdot \mathbf{J}_b$, single-particle anisotropy $(\hat{R}_{ab} \cdot \mathbf{J}_a)^2$, pseudo-dipolar terms $(\hat{R}_{ab} \cdot \mathbf{J}_a)(\hat{R}_{ab} \cdot \mathbf{J}_b)$, and unusual anisotropic terms which are quartic in the components of the $\mathbf{J}$'s.

For more than one electron or hole, this straightforward derivation becomes cumbersome; in Appendix 4 it is shown that the form (43) is valid for an arbitrary number of localized electrons, the C_i being simply related to coefficients computed there. Table I lists the quantities

$$P_i = -\frac{5C_i\beta_i}{2\alpha_J{}^2(2\lambda+3)(2\lambda-1)} \quad (43b)$$

for the triply ionized heavy rare earths; here $\beta_1 = \beta_2 = 1$ and $\beta_3 = -2J^2$, so that $P_i K_2(R)/K_0(R)$ measure the ratios of the various terms in H_2 to the zero-order isotropic terms of Eq. (31).

To calculate K_n we need the radial $4f$ function which enters into the radial integrals $\mathcal{J}(q l \lambda)$. Using the value 45 for the screening parameter[23] gives $q_0 r_0 \sim 0.89$ for

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[23] Using the same screening parameter σ for Gd, r_0 is considerably larger than the corresponding maximum in the Hartree-Fock (HF) radial function [R. E. Watson and A. J. Freeman, Phys. Rev. Letters 6, 277 (1961)]. If we simply fitted r_0 to the position of the HF function, our estimates would be altered appreciably. However, the peak of such a hydrogenic function is considerably narrower than that of the HF function; a rough estimate shows that this broadening of the HF function approximately compensates the effect of the change in location of the maximum. Further, the screening parameter chosen for the best fit to form

Tb, where r_0 is the location of the maximum in $R(r)$. With the help of the expressions in Appendix 2, we obtain $b_0 \cong -4.2$, $b_2 \sim 0.1$, and $\gamma_2/\gamma_0 \cong 0.21$; using the value of R connecting one site to its nearest neighbor in the adjacent c plane, we then find that $K_2/K_0 \cong 0.14$. This ratio decreases in going from Tb towards Tm because of the contraction of the $4f$ shell. However, this change is small (we find $K_2/K_0 \cong 0.10$ for Tm) so that roughly

$$K_2/K_0 \approx 0.1.$$

Referring to Table I, we see that for Tb through Er, the single-particle terms and the fourth-order terms give $P_i(K_2/K_0) \approx 10\%$, whereas for Tm they are $P_3(K_2/K_0) \approx 30\%$ and $P_1(K_2/K_0) \approx 80\%$. The dipolar terms ($P_2$) are always much smaller, running around 1%.

One somewhat surprising aspect of these numbers is that the size of H_2 depends strongly on the number of $4f$ electrons, rather than depending only on the value of $k_F r_0$ as might have been suspected.[5] Indeed, the first correction term for Tm is of the same order of magnitude as the zeroth term, but for the other elements it is only $\sim 10\%$, whereas $k_F r_0$ decreases as the number of $4f$ electrons increases. Now it turns out that the single-particle terms (which, for a single pair of triply ionized rare-earth atoms in the conduction electron sea, are $\sim P_1 K_2/K_0$ times the zero-order term) are reduced in the metal: They are proportional to $\sum_b K_2(R_{ab})(\hat{R}_{ab} \cdot \mathbf{J}_a)^2$; although we did not obtain the order of magnitude of this sum (after summing out to 12th neighbors there was no sign of convergence), we did find that the sum reduces the single-particle terms by at least an order of magnitude,[24] so that they are small for the rare-earth metals. However, because this reduction is due to symmetry,[24] our results suggest that large deviations in behavior from that predicted on the basis of the usual isotropic expression should be observable in the magnetic properties of a dilute alloy of Tm in La.[25]

The aspect of the present computation that is independent of the choice of band functions or localized orbitals is the atomic parameters P_i. The value of K_2/K_0, on the other hand, depends on our choice of free electron functions. Hence, our result that the anisotropic exchange forces, in particular the fourth-order terms, are of the order of 10% of the isotropic terms, is strictly tentative; it strongly suggests that

such terms should be investigated further on the basis of improved band functions.

V. ASPECTS OF THE MAGNETIC ORDERING IN THE HEAVY RARE-EARTH METALS

A. Isotropic Interaction Parameters

We calculate here the interaction parameters in H_0, despite the questionable use of free-electron band functions and second-order perturbation theory, since comparison with the observed Curie temperatures and spiral wavelengths gives a rough check on the basic approximations. Writing (31) as

$$H_0 = -\sum_{a,b} A(R_{ab}) \alpha_J^2 \mathbf{J}_a \cdot \mathbf{J}_b, \qquad (44)$$

we find, for nearest neighbors in Gd (using the f hydrogenic function with $Z = 19$),

$$A(R_1) \cong 0.75°K. \qquad (45)$$

[If the previous approximation[4] had been used in place of the more accurate expression (28), this would have been larger by a factor of about 2.5.] Since $\alpha_J = 1$ and $J = 7/2$ for Gd, this gives a Curie temperature of $\sim 100°K$ using molecular field theory for nearest-neighbor interactions. This is certainly satisfactory agreement in view of the crudity of our band functions (the observed result is $290°K$). Although this might very well turn out to be fortuitous, it is perhaps worth mentioning that one would expect better band functions to concentrate more charge near the atomic core, thus giving a tendency to increase the band-local exchange (which depends mainly on the behavior of the band functions near the maximum in the $4f$ radial function) and hence the calculated Curie temperature.

We also looked at more distant interactions. To do this we considered configurations in which all $\mathbf{J}_c$ are parallel within any one c plane (as is observed for all the rare earths that have been studied[6]). Then one can define effective interplanar interactions[7,8] A_ν, where A_1 is the interaction between nearest-neighbor c planes, etc. We find A_1 positive, A_2 negative, and A_ν negligible for $\nu > 2$, with

$$t = -4A_2/A_1 \gtrsim 1, \qquad (46)$$

[for gadolinium we found $t \cong 1.4$; the Ruderman-Kittel potential, Eq. (33) with $b_0 = 0$, gives $t \sim 1.8$]. Remembering that when $t > 1$ the Hamiltonian of Eq. (46), treated classically, is minimized by a simple spiral,[26] we see that (44) with (28) predicts a *spiral ground state* (with wavelength ≈ 10 layers, somewhat shorter for the R-K potential[27]). This, of course, appears to be in violent disagreement with experiments which suggest that Gd is ferromagnetic. Although there is

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factor measurements is roughly constant from Gd to Er [(W. C Koehler and E. O. Wollan, Phys. Rev. **92**, 1380 (1953); W. C. Koehler, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **110**, 37 (1958); A. J. Freeman (private communication)]. Hence, uncertainties in the atomic functions give only minor uncertainties in the present considerations.

[24] This large decrease is due to the fact that for the perfect hcp lattice, the J-dependent part of the sum over b vanishes for the first few neighbors (though not for all).

[25] In analyzing such an experiment, one would, of course, include crystalline anisotropy, as discussed in reference 8.

[26] D. H. Lyons and T. A. Kaplan, Phys. Rev. **120**, 1580 (1960).

[27] This result is consistent with the fact that the ordinary Ruderman-Kittel theory predicts the ferromagnetic state to be unstable as shown by E. J. Woll, Jr., and S. J. Nettel, Phys. Rev. **123**, 796 (1961).

little reason to be concerned over this apparent discrepancy (again because of the crudity of our band functions), it is interesting to note that the discrepancy is probably much smaller than appears at first sight. The reason is that since the neighboring elements (Tb, Dy, $\cdots$) all show spirals, with wavelength increasing as Z decreases,[6] one expects that t should be of the order of 1 for Gd,[28] with $A_1 > 0$, $A_2 < 0$ (as the latter apparently are [7-9] in Tb, $\cdots$), as found above.

Concerning the other rare-earth metals, Tb through Tm, we first point out that t increases slightly, t being $\cong 1.6$ for Tm. This variation comes about through variation in b_0, Eq. (28) [which causes a change in the *shape* of $K_0(R)$], the change in b_0 being caused by the contraction of the $4f$ shell. (For our model we find $q_0 r_0 = 2k_F r_0$ goes from 0.93 for Gd to 0.76 for Tm.) The observed[6] wavelength of 7 layers found in Tm and the high-temperature phase of Er corresponds exactly to the calculated value $t = 1.6$. This agreement is, of course, *too* good to be taken seriously; nevertheless, we see that for the heavy rare earths including Gd the crude theory gives values of t that are of the right order of magnitude and sign, and gives the change in t from element to element in qualitative agreement with experiment.

At first sight, one might expect the variation in $A(R)$ with atomic number found here might spoil the agreement, found on the paramagnetic Curie temperature by de Gennes,[29] between theory with fixed $A(R)$ and experiment. This is particularly so when one notes that for small enough $q_0 r_0$, $A(R) \propto (q_0 r_0)^4$ [Eq. (28) with Eq. (3.1)]; however, the series multiplying $11 r_0^2/9$ in (3.1) reduces this variation effectively to $(q_0 r_0)^2$. Although the latter variation changes de Gennes' results, computations show that it does not alter the fact that there remains semiquantitative agreement with the trend of these experimental results.

B. Thermal Variation of Spiral Wavelength

Miwa and Yosida[9] and Elliott[8] attempted to explain the observed[6] thermal variation in spiral wavelength by means of quadrupolar interactions H_Q. We consider only the "first principles" calculation of reference 9, and confine ourselves to the case of Dy as was done there. The authors[9] found that although the direct quadrupolar interaction gave the spiral wave vector Q varying approximately linearly with T, as observed,[6] the calculated slope was about a factor of 40 too small. They then suggested that indirect quadrupolar coupling (which would have the same functional dependence on

the spins but with a different coefficient) might alter the situation favorably. However, this is not reasonable, since the direct quadrupolar terms considered[9] were already $\approx 10\%$ of the isotropic terms; i.e., if they were increased by a factor of 40, they would be unreasonably large. This suggests that possibly anisotropic interactions of a different form might account for the facts.

Accordingly, we investigate the effect on spiral wavelength of the anisotropy terms of Eq. (43), following the molecular field approach used in reference 9. It will be seen that for Dy, in which the moments lie in the basal plane, only the fourth-order terms influence the spiral wave vector Q. Again taking the average moments to be parallel within any basal plane, our fourth-order terms may be written

$$H_A = 2 \sum_{\nu\mu} A_{\nu\mu}{}^{(2)} J_{\nu z}{}^2 \mathbf{J}_\nu \cdot \mathbf{J}_\mu,$$

where ν, μ refer to the various basal planes and $J_{\nu z}$ is the component of $\mathbf{J}_\nu$ along the c axis; $A_{\nu\mu}{}^{(2)}$ are roughly of the order of $2\alpha_J{}^2 P_3 K_2(R_{ab})$. Calculating the thermal average $\langle H_A \rangle$ in the molecular field approximation, with the $\langle \mathbf{J}_\mu \rangle$ forming a spiral with moments perpendicular to the c axis, we get

$$\langle H_A \rangle = \sigma J^2 \left[\frac{J(J+1)}{J^2} - \frac{\langle J_z{}^3 \rangle}{\sigma J^2} \right] \equiv \sigma J^2 F(T),$$

where $\sigma = |\langle J_\mu \rangle|$. Following reference 9, we then find

$$Q(T)c' - Q_0 c' = \frac{A_2'(Q_0) J^2/c'}{-J''(Q_0)/c'^2} F(T),$$

where $A_2(Q)$ is the Fourier transform of $A_{\nu\mu}{}^{(2)}$, $Q(T)$ is the wave vector at temperature T, Q_0 is the wave vector in the absence of H_A, and c' is the interlayer distance. As for $\langle H_Q \rangle$,[9] we find that $F(T)$ varies approximately linearly over a large range, the change in $F(T)$ for T going from about $\frac{1}{2} T_N$ to T_N being about 0.1. Assuming that $A_2'(Q_0)/c' \approx A_2(Q_0)/c'^2$ and $J''(Q_0)/c'^2 \approx J(Q_0)$ (the latter is found to be true in reference 9), then the results of the previous section suggest that $A_2'(Q_0) J^2 c'/J''(Q_0)$ $\approx 10^{-1}$. Hence, the change in $Q(T)c'$ from $\frac{1}{2} T_N$ to T_N is calculated as $\approx 10^{-2}$, whereas the observed change is about a factor of 35 larger. To increase the calculated value appropriately, one would need $A_2'(Q_0)/c'$ $\gg A_2(Q_0)$; such a requirement is not satisfied with the R dependence of the interactions calculated in this paper, and is unlikely in any case.

Speaking generally, it would in our opinion be surprising if there existed an anisotropic interaction of some other form, consistent with the experimental fact that it must be small ($\sim 10\%$) compared with the isotropic exchange, that would somehow give a thermal variation in Q that is some 40 times larger than that given either by the interaction just considered or the quadrupolar interaction. In other words, it is our

[28] This is apparently supported by the recent low-field measurements of K. P. Belov and A. V. Ped'ko, Soviet Phys.—JETP **15**, 62 (1962), who found a ferromagnetic-antiferromagnetic transition at fields ≈ 10 G. This implies that t is greater than but very close to 1; by considering only exchange and external field energies, we estimate crudely that $t - 1 \approx 10^{-2}$, so that the wavelength ≈ 50 layers.

[29] P. G. de Gennes, Compt. Rend. **247**, 1836 (1958).

feeling that one should consider the possibility of thermal variation of the exchange integrals, $A(R)$ [Eq. (44)] themselves.[30] Possible sources of such a variation, other than the negligible effect of thermal expansion of the lattice are as follows:

(a) Thermal variation of the band wave functions and energies due to their exchange interaction with the long-range-ordered localized moments.

(b) Magnetostriction. In other words, in the usual theory the effective Hamiltonian is calculated considering the nuclear positions fixed at their equilibrium values; i.e., the lattice is in its ground state. However, in the second-order perturbation theory the initial and final states should include thermally excited phonon states, and the virtual or intermediate states should also include excited phonon states, the latter contributing because of the fluctuation in the R_b, Eq. (2).

These effects are under investigation.

VI. SUMMARY AND DISCUSSION

By expanding the band wave functions in spherical harmonics, essentially following Liu,[1] we have shown that band-local exchange forces give rise (in second-order perturbation theory) to isotropic and anisotropic corrections to the usual isotropic interaction between localized atomic moments. The first correction term was examined in some detail. It included single-atom forces quadratic in the atomic angular momenta, J_a; bilinear interactions in the form of pseudodipolar terms; and unusual two-atom forces which are quartic in the J's that are linear for one site, cubic for the other. Higher correction terms will include pseudoquadrupolar forces among others. It should be noted that these anisotropy forces arise from the fact that the atomic orbital angular momentum L is not zero and there is strong intra-atomic spin-orbit coupling. The total atomic angular momentum per atom, J, was taken to be a good quantum number in accordance with the assumption that intra-atomic spin-orbit forces≫crystal field effects (valid for the rare-earth metals), and this is the only way that spin-orbit forces enter into the terms calculated here. Intuitively, these anisotropies, which relate the moment directions for a pair of atoms a, b to the line connecting a and b, can occur because conduction electrons scattered from a and traveling to b "feel" the orientation of the nonspherical atomic charge clouds relative to the line a-b.

The above conclusions as to the form of the indirect exchange interaction operator depend only on the standard assumptions[2-5] as to the unperturbed band and atomic wave functions.[31]

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[30] This was considered phenomenologically by U. Enz, Physica 26, 698 (1960).

[31] These assumptions exclude the possibility of using as unperturbed band states Overhauser's spin-density wave states [J. Phys. Chem. Solids 13, 71 (1960)]. For example, the latter are not Bloch functions (i.e., they do not have translational symmetry).

A rough estimate for rare-earth metals was obtained by using the free-electron model for the unperturbed band states and screened hydrogenic atomic functions. The results, already summarized in Sec. I, suggest that the usual assumption, in which the zero-order isotropic term is taken to dominate the anisotropic exchange terms, is reasonable for the heavy rare-earth metals, but would be quite questionable for, e.g., a dilute alloy of Tm in La. Even in the former case, the calculated size of the anisotropic exchange terms suggests that these terms might contribute appreciably to the anisotropy properties of these metals.

The same model was also used to investigate the zero-order isotropic terms in the heavy rare-earth metals, and was found to give the interaction parameters in the right order of magnitude, both with respect to the predicted Curie temperatures and the observed spiral wavelengths.

Although this agreement suggests that the free electron model for the unperturbed band functions and the use of second-order perturbation theory might not be bad approximations, it is also quite possible that the agreement is only fortuitous. Hence, we must emphasize the point that the order-of-magnitude estimates given here are meant to be only suggestive.

The thermal variation in Dy of spiral wave vector Q, due to anisotropic terms of the form calculated here was also investigated. Taking these terms to be of a reasonable size ($\sim 10\%$ of the isotropic terms), we found that the variation of Q is more than an order of magnitude too small. Since quadrupolar interactions were found to be similarly inadequate by Miwa and Yosida,[9] we were tempted to conclude that attempts to explain this phenomenon by a spin Hamiltonian with temperature-independent coefficients[7-9] are unlikely to succeed. Some possible sources of thermal variation of the exchange parameters, $A(R)$, were pointed out.

ACKNOWLEDGMENTS

APPENDIX 1

The Half-Filled-Shell Case

The simplest way to derive the exchange operator when the atomic shell is half-filled is to note in Eq. (1) that $\psi_{JM}(1\cdots n)$ is a product of a space state $\psi(r_1\cdots r_N)$ (with $L^2=0$), and a spin state (of maximum multiplicity). Then, using the Dirac identity for the pair permutation of spins, one immediately obtains the well-known result that the indirect exchange matrix element is $-I(\mathbf{k},\mathbf{k}')\langle JM'\sigma|n/2+\mathbf{S}\cdot\mathbf{s}|JM\sigma\rangle$, where $\mathbf{s}$ is

the conduction electron spin and

$$I(\mathbf{k'k}) = \psi^*(\mathbf{r}_1\cdots\mathbf{r}_n)\phi_{\mathbf{k'}}^*(\mathbf{r})\,|\,\mathbf{r}_1-\mathbf{r}\,|^{-1}\psi(\mathbf{r},\mathbf{r}_2\cdots\mathbf{r}_n)$$

$$\times\phi_{\mathbf{k}}(\mathbf{r}_1)d\mathbf{r}_1\cdots d\mathbf{r}_n d\mathbf{r} \quad (1.1)$$

$$=\frac{1}{2\lambda+1}\sum_{m=-\lambda}^{\lambda}\int d\mathbf{r}d\mathbf{r'}\;\phi_{\mathbf{k'}}^*(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r'})$$

$$\times\chi_{\lambda m}(\mathbf{r})\chi_{\lambda m}^*(\mathbf{r'})\,|\,\mathbf{r}-\mathbf{r'}\,|^{-1}; \quad (1.2)$$

the second form was obtained by using the explicit form of $\psi(\mathbf{r}_1\cdots)$ in terms of the single-particle atomic functions χ. Using the general expansion (6) and the expansion of $|\mathbf{r}-\mathbf{r'}|^{-1}$ in spherical harmonics, one obtains an expression for (1.2) involving integrals of products of three spherical harmonics. Expressing the latter in terms of the Clebsch-Gordan coefficients and taking advantage of an orthogonality property of these coefficients,[13] we find

$$I(\mathbf{k'},\mathbf{k}) = \sum_{L=0}\sum_{l=0} F(lL;\mathbf{k'},\mathbf{k})C^2(\lambda lL;00), \quad (1.3)$$

where

$$F(lL;\mathbf{k'},\mathbf{k}) = \frac{1}{2L+1}\sum_{M=-L}^{L}\int d\mathbf{r}d\mathbf{r'}\;r^2r'^2\frac{r_<^l}{r_>^{l+1}}R(r)R(r')$$

$$\times B_{LM}(\mathbf{k'},r)^*B_{LM}(\mathbf{k},r). \quad (1.4)$$

This is an exact expansion suitable as a starting point for calculations based on general band functions. Note that $\mathcal{J}(\mathbf{k'},\mathbf{k})$ appearing in Eq. (8) is the term in (1.3) for $L=0$; the remaining terms contribute to the coefficient $I(\mathbf{k'},\mathbf{k})$ of $\mathbf{S}\cdot\mathbf{s}$, but add no new operators.

For free band electrons, (1.4) becomes

$$F(lL;\mathbf{k'},\mathbf{k}) = \frac{(4\pi)^2}{\Omega(2L+1)}\sum_{M=-L}^{L}Y_{LM}^*(\hat{k}')$$

$$\times Y_{LM}(\hat{k})\mathcal{J}(k'k,LLl), \quad (1.5)$$

where $\mathcal{J}(\cdots)$ is defined in Eq. (14). In the text we approximated $I(\mathbf{k'},\mathbf{k})$ by $I(0,\mathbf{q})$ ($\mathbf{q}=\mathbf{k}-\mathbf{k'}$), giving an intuitive justification based on the effect of $|\mathbf{r}_1-\mathbf{r}|^{-1}$ in (1.1). Since $1/r$ is not a very strong singularity, however, this justification is open to some question. One way of testing this approximation is to approximate (1.5) by another function of $\mathbf{q}$ alone. For example, if we put $\mathbf{p}=\mathbf{k}+\mathbf{k'}$, then $\phi_{\mathbf{k'}}^*(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r'}) \propto \exp[\frac{1}{2}i\mathbf{p}\cdot(\mathbf{r'}-\mathbf{r})]$ $\times\exp[\frac{1}{2}i\mathbf{q}\cdot(\mathbf{r'}+\mathbf{r})]$, suggesting that the integral is a slowly varying function of $\mathbf{p}$, and that we can put $\exp[\frac{1}{2}i\mathbf{p}\cdot(\mathbf{r'}-\mathbf{r})]\sim 1$. This is equivalent to writing $I(\mathbf{k'},\mathbf{k})\sim I(-\mathbf{q}/2,\mathbf{q}/2)$, which is, of course, a different function than $I(0,\mathbf{q})$. Equation (1.5) gives

$$I(-\tfrac{1}{2}\mathbf{q}, \tfrac{1}{2}\mathbf{q}) = \frac{4\pi}{\Omega}\sum_{Ll}(-)^L\mathcal{J}(\tfrac{1}{2}q,\tfrac{1}{2}q,LLl)C(llL;00); \quad (1.6)$$

we evaluated this as a series in powers of q^2 and found

that the first four coefficients differ from those of $I(0,q)$ (see Appendix 2) by less than 5%. This further justifies our assumption that $I(0,q)$ is a sufficiently good approximation to $I(\mathbf{k},\mathbf{k'})$. Actually, one can give a strong independent argument that, as far as the effective interactions (19) between localized moments are concerned, (1.6) is a very good approximation to $I(\mathbf{k'},\mathbf{k})$.

APPENDIX 2

Evaluation of the K Integrals of Eq. (26)

Noting that for the rare earths $R \gtrsim 3.5$ Å and $q_0 = 3$ Å^{-1}, one can see that R_{min} is large in the sense that $j_L(qR)$, for small L, oscillates rapidly over the region $(q \lesssim q_0)$ in which the rest of the integrand is large. This suggests that we look for an expansion in powers of $1/R$. To this end, first consider

$$K(R,000) \equiv K_0(R) = R^{-1}\,\mathrm{Im}\left\{\int_0^{q_0}dq\;qf_+(q/q_0)\gamma_0(q)e^{iqR}\right.$$

$$\left.+\int_{q_0}^{\infty}dq\;qf_-(q/q_0)\gamma_0(q)e^{iqR}\right\} \quad (2.1)$$

$$\equiv R^{-1}\,\mathrm{Im}(I_++I_-)$$

with

$$f_\pm(x) = 1 + \frac{1-x^2}{2x}\ln\left(\pm\frac{1+x}{1-x}\right), \quad (2.2)$$

and

$$\gamma_0(q) = \mathcal{J}^2(q0\lambda). \quad (2.3)$$

Considering the two integrals in (2.1) separately, in the complex q plane, we see that the functions $f_\pm(q/q_0)$ are analytic except for the branch point at $q=q_0$ (and $-q_0$). The other controlling factor on possible distortions of the contour is the singularities of $\gamma_0(q)$ for which we consider the following models.

If $R(r)$ were sharply peaked at r_0 then (2.3) would give $\gamma_0(q)$ proportional to $(\sin^2 qr_0)/q^2$. This is analytic so that I_+ is equal to the integral over $C_1+C_2+C_3$ and I_- is "C_4+C_5" in the limit $\rho\to\infty$ (see Fig. 1). Further, the integrals over C_2 and C_5 would vanish as $\rho\to\infty$ since $r_0 < R[f(x)\to 0$ as x^{-2} when $|x|\to\infty]$. In addition
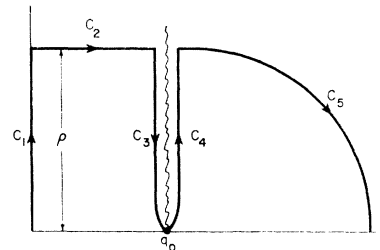

FIG. 1. Contours in q plane for evaluating $K(R)$.

the integral over C_1 can easily be seen to be real so that

$$K_0(R) = R^{-1} \operatorname{Im} \left\{ \int_{C_3} dq \ q f_+ \gamma_0(q) e^{iqR} \right.$$

$$\left. + \int_{C_4} dq \ q f_- \gamma_0(q) e^{iqR} \right\};$$

C_3 and C_4 are supposed to be vertical lines lying infinitesimally to the left and right, respectively, of the branch cut at $\operatorname{Re} q = q_0$, as shown. If f_+ and f_- were analytic, then K_0 would vanish; in fact,

$$K_0(R) = R^{-1} \operatorname{Im} \left\{ \int_{C_3} dq \ q \frac{1 - (q/q_0)^2}{2(q/q_0)} \ln\left(\frac{1}{q_0 - q}\right) e^{iqR} \right.$$

$$+ \int_{C_4} dq \ q \frac{1 - (q/q_0)^2}{2(q/q_0)} \ln\left(\frac{1}{q - q_0}\right) e^{iqR} \right\}$$

$$= \frac{\pi}{2q_0 R} \operatorname{Im} \left\{ e^{iq_0 R} \int_0^\infty dy \ \gamma_0(q_0 + iy) \right.$$

$$\left. \times (y^2 - 2iq_0 y) e^{-yR} \right\}, \quad (2.4)$$

obtained by using the proper branch of $\ln(q_0 - q)$ on C_3 and $\ln(q - q_0)$ on C_4. From this expression it is immediately apparent that it is the behavior of $\gamma_0(q)$ in the neighborhood of q_0 that determines the behavior of $K_0(R)$ for large R—this is, of course, due to the singularity in $f(x)$ at $x = 1$ [although $f(x)$ is continuous, its first derivative is not]. By expanding $\gamma_0(q_0 + iy)$ in powers of iy, (2.4) readily yields the desired expansion of $K_0(R)$ in powers of R^{-1} (times trigonometric functions of $q_0 R$). The same procedure also gives

$$K(R, 202) \equiv K_2(R)$$

$$= -K_0'(R) + \frac{\pi}{2q_0 R} \left\{ \frac{3}{R^2} \operatorname{Im} e^{iq_0 R} \right.$$

$$\times \int_0^\infty dy \frac{\gamma_2(q_0 + iy)}{(q_0 + iy)^2} (y^2 - 2iq_0 y) e^{-yR}$$

$$- \frac{3}{R} \operatorname{Re} e^{iq_0 R} \int_0^\infty dy \frac{\gamma_2(q_0 + iy)}{q_0 + iy}$$

$$\left. \times (y^2 - 2iq_0 y) e^{-yR} \right\}, \quad (2.5)$$

where

$$\gamma_2(q) = \mathcal{G}(q0\lambda)\mathcal{G}(q2\lambda),$$

and $K_0'(R)$ is given by (2.4) with γ_0 replaced by γ_2.

As another, more realistic, example for $\gamma_0(q)$ we take the radial function to be hydrogenic, $Cr^\lambda \exp(-\alpha r)$. It can then be shown (see Appendix 3) that $\gamma_0(q)$ has poles at $q = \pm i\alpha$, $\pm 2i\alpha$ (of order 2 and $4\lambda + 6$, respectively), and $\gamma_0(q) \to 0$ as $|q| \to \infty$. Hence, the only change needed in the contour of Fig. 1 is that C_1 go around (to the right of) these poles. Letting C_1 be along the imaginary axis, except for detours in the form of small semicircles at $i\alpha$ and $2i\alpha$, it is easy to see that one will get (2.4) plus the contributions from these semicircles, the latter being proportional to $\exp(-\alpha R)$ and $\exp(-2\alpha R)$, respectively. Since $\alpha = \lambda/r_0$ where r_0 is location of the maximum in $r^\lambda \exp(-\alpha r)$, and since $R/r_0 \approx 10$ for nearest neighbors in the rare-earth metals, for which $\lambda = 3$, these contributions are completely negligible. Hence, it is reasonable to assume that (2.4) and (2.5) are accurate at large R for physical radial wave functions.

Equations (2.4) and (2.5) readily give Eq. (28) of the text.

APPENDIX 3

The Radial Integrals

We evaluate

$$\mathcal{G}(ql\lambda) = \int dr_1 dr_2 \ r_1^2 r_2^2 \frac{r_<^\lambda}{r_>^{\lambda+1}} R(r_1) R(r_2) j_l(qr_1),$$

where

$$R(r) = \left[\frac{(2\alpha)^{2\lambda+3}}{(2\lambda+2)!}\right]^{1/2} r^\lambda e^{-\alpha r} = a_\lambda r^\lambda e^{-\alpha r}.$$

One has

$$\mathcal{G}(ql\lambda) = A_l + B_l,$$

where

$$A_l = a_\lambda^2 \int_0^\infty dr \ r^{2\lambda+2} e^{-\alpha r} \int_r^\infty dr' \ r' e^{-\alpha r'} j_l(qr'),$$

$$B_l = a_\lambda^2 \int_0^\infty dr \ r^{2\lambda+2} e^{-\alpha r} j_l(qr) \int_r^\infty dr' \ r' e^{-\alpha r'}.$$

Using the expansion of $j_l(x)$ in powers of x, one straightforwardly finds

$$A_l = \frac{1}{\alpha^2}\left(\frac{2q}{\alpha}\right)^l \sum_{m=0}^\infty \frac{(-)^m(l+m)!(2m+l+1)!}{m!(2l+2m+1)!}\left(\frac{q}{\alpha}\right)^{2m} \sum_{s=0}^{2m+l+1} \frac{(2\lambda+2+s)!}{s!2^s(2\lambda+2)!},$$

$$B_l = \frac{1}{2\alpha^2}\left(\frac{q}{\alpha}\right)^l \sum_{m=0}^\infty \frac{(-)^m(l+m)!(l+2\lambda+2m+2)!(l+2\lambda+2m+5)}{4^m m!(2l+2m+1)!(2\lambda+2)!}\left(\frac{q}{\alpha}\right)^{2m}.$$

Putting

$$qr_0 = x,$$

where $r_0 = \lambda/\alpha$ [the location of the maximum in $R(r)$], we find for $\lambda = 3$,

$$\mathcal{G}(q,0,3) = (11r_0{}^2/9)(1 - 0.624x^2 + 0.174x^4 \\ - 0.033x^6 + \cdots), \quad (3.1)$$

$$\mathcal{G}(q,2,3) = (0.305)r_0{}^2 x^2 (1 - 0.518x^2 + 0.107x^4 \\ - 0.017x^6 + \cdots). \quad (3.2)$$

An alternate form for $\mathcal{G}(q,0,\lambda)$ can be obtained easily by using $j_0(x) = (\sin x)/x$. This is

$$\mathcal{G}(q,0,\lambda) = \frac{(2\alpha)^{2\lambda+3}}{q} \operatorname{Im}\left\{ \left(\frac{2\alpha + iq}{4\alpha^2 + q^2} \right)^{2\lambda+2} \right.$$
$$\left. \times \left[\frac{(\alpha+iq)(2\alpha+iq)}{(\alpha^2+q^2)(4\alpha^2+q^2)} + \frac{1}{2(\lambda+1)\alpha^2} + \frac{1}{2}\frac{2\alpha+iq}{4\alpha^2+q^2} \right] \right\}, \quad (3.3)$$

which shows directly the analytical structure of $\mathcal{G}$ for all q.

APPENDIX 4

Operator Equivalents for Partially Filled Shells

In this Appendix we give operator equivalents (constructed from the total angular momenta $\mathbf{J}^a$ and $\mathbf{J}^b$) to the operator

$$[\tfrac{1}{2} + 2\mathbf{s}^a(1) \cdot \mathbf{s}^b(1)] Y_{20}{}^a(1) \quad (4.1)$$

which appears in the correction term H_2, Eq. (32). Within the set of states we consider, for which $\mathbf{J}^a \cdot \mathbf{J}^a$ and $\mathbf{J}^b \cdot \mathbf{J}^b$ are constant, the operator is equivalent to a linear combination of irreducible tensors[13] built up from those in Table II. The operators in Table II result from coupling J with itself:

$$\mathcal{G}_{k\mu} = \sum_m C(1\,k - 1\,k; \mu - m, m) J_{\mu-m}\mathcal{G}_{k-1,m}, \quad (4.2)$$

where the $J_\nu \equiv \mathcal{G}_{1\nu}$ are the "spherical" components of $\mathbf{J}$. Later we use this notation for the spherical components of spin operators. The $C(j_1 j_2 j; m_1 m_2) \equiv C(j_1 j_2 j; m_1 m_2 m)$ are the usual Clebsch-Gordan coefficients.

We begin by noting that equivalent operators must be composed of irreducible tensors of the same rank and components with respect to any of the three angular momenta $\mathbf{J}^a$, $\mathbf{J}^b$ and $\mathbf{J}^a + \mathbf{J}^b$. This requirement, plus one parity consideration suffices to determine the form of the equivalences (4.3) through (4.6):

$$Y_{20}{}^a(1) \equiv A\mathcal{G}_{20}{}^a, \quad (4.3)$$

$$s_\mu{}^b(1) \equiv BJ_\mu{}^b, \quad (4.4)$$

$$Y_{20}{}^a(1)s_\mu{}^a(1) \equiv C_\mu{}^{(1)}J_\mu{}^a + C_\mu{}^{(3)}\mathcal{G}_{3\mu}{}^a, \quad (4.5)$$

$$Y_{20}{}^a(1)\mathbf{s}^a(1) \cdot \mathbf{s}^b(1) = Y_{20}{}^a(1) \sum (-)^\mu s_\mu{}^a(1)s_{-\mu}{}^b(1)$$
$$\equiv D^{(1)}\mathcal{G}_{20}{}^{ab} + D^{(3)}\mathcal{G}_{20}{}^{ab}, \quad (4.6)$$

TABLE II. Irreducible tensor angular momentum operators.

k, μ		$\mathcal{G}_{k\mu}$
1	0	J_z
1	± 1	$\mp (1/\sqrt{2})(J_x \pm iJ_y)$
2	0	$(1/\sqrt{6})(3J_z{}^2 - \mathbf{J} \cdot \mathbf{J})$
2	± 1	$\mp \tfrac{1}{2}(2J_z \mp 1)(J_x \pm iJ_y)$
2	± 2	$\tfrac{1}{2}(J_x \pm iJ_y)^2$
3	0	$(1/\sqrt{10})(5J_z{}^2 - 3\mathbf{J} \cdot \mathbf{J} + 1)J_z$
3	± 1	$\mp(\sqrt{3}/2\sqrt{10})[5J_z(J_z \mp 1) - \mathbf{J} \cdot \mathbf{J} + 2](J_x \pm iJ_y)$
3	± 2	$(\sqrt{3}/2\sqrt{2})(J_z \mp 1)(J_x \pm iJ_y)^2$
3	± 3	$\mp(1/2\sqrt{2})(J_x \pm iJ_y)^3$

where

$$\mathcal{G}_{20}{}^{ab} \equiv \sum_\mu C(112; \mu - \mu)J_\mu{}^a J_{-\mu}{}^b$$
$$= (1/6^{1/2})(3J_z{}^a J_z{}^b - \mathbf{J}^a \cdot \mathbf{J}^b), \quad (4.7)$$

and

$$\mathcal{G}_{20}{}^{ab} \equiv \sum C(312; \mu - \mu)\mathcal{G}_{3\mu}{}^a J_{-\mu}{}^b \quad (4.8)$$

$$= -\frac{1}{2(35)^{\frac{1}{2}}}\{5\mathcal{G}_{20}{}^a \mathbf{J}^a \cdot \mathbf{J}^b + 5\mathbf{J}^a \cdot \mathbf{J}^b \mathcal{G}_{20}{}^a$$
$$+ \mathcal{G}_{20}{}^{ab}(3 - 4\mathbf{J}^a \cdot \mathbf{J}^a)\}. \quad (4.9)$$

Some remarks on (4.3) thru (4.9) now follow. First, we note that

$$r^2(1)Y_{20}(1) = \frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}[3z^2(1) - r^2(1)]. \quad (4.10)$$

Now Stevens[32] computed by a different method, the operator equivalence

$$\sum_i [3z^2(i) - r^2(i)] \equiv \alpha \langle r^2 \rangle_{av}[3J_z{}^2 - J(J+1)] \quad (4.11)$$

for the ground states of all triply ionized rare-earth ions. We could, therefore, compute A by using the relation

$$A = \frac{1}{4n}\left(\frac{5}{\pi}\right)^{1/2}\alpha, \quad (4.12)$$

where n is the number of electrons in the $4f$ shell. Instead, we compute A separately and use (4.12) to check our result. The main step to compute A is also necessary for the computation of the remaining operator equivalents anyhow. The computation is more concise than that of Stevens, and results in a closed formula for A (or α) which applies to all Hund's rule states.

Relation (4.4) is, of course, well known in the form

$$S_\mu \equiv (g-1)\mathbf{J}_\mu \quad (4.13)$$

so that $B = (g-1)/n$, where g is the Landé g factor. We put down (4.4) for completeness.

Regarding (4.5), we note that since Y_{20} is of rank two and s_μ is rank one, we can expect, by the triangular conditions, that the right-hand side will be a linear

[32] K. W. H. Stevens, Proc. Phys. Soc. (London) 65, 209 (1951)

combination of rank one, rank two, and rank three irreducible tensors. However, we shall see that the rank-two part vanishes by reasons of parity. The μ dependence of the coefficients C_μ and D_μ must be such that, when (4.5) is combined with (4.4) according to the first half of (4.6), the result is the zeroth component of some tensor of rank two with respect to simultaneous rotations of the coordinates of all particles at both sites. This must be so since $\mathbf{s}^a(1)\cdot\mathbf{s}^b(1)$ is a scalar with respect to such rotations.

Given the definitions (4.7) and (4.8), the right-hand side of (4.6) should be clear. We have cast the expression for $\mathcal{G}_{20}{}^{ab}$ in the form (4.9) in order to compare the

general results with the results given in the body of the paper for one electron and one hole. Equation (4.9) is straightforward but tedious to verify.

The Multipliers A, $C_\mu{}^{(k)}$, $D_\mu{}^{(k)}$

The states $|\gamma LSJM\rangle$ of maximum S for $n\leq 2l+1$ are particularly simple since they are formed by a simple vector coupling of spatial states $|\gamma_1 LM_L\rangle$ with spin states $|\gamma_2 SM_s\rangle$. (The γ's stand for all other quantum numbers needed to specify the states.) In this case, straightforward application of known results[33,34] in the theory of angular momentum quickly gives

$$A = \frac{(-)^{L+S+J}(2J+1)(\gamma_1 L\|Y_2\|\gamma_1 L)\begin{Bmatrix} L & J & S \\ J & L & S \end{Bmatrix}}{(J\|\mathcal{G}_2\|J)}, \tag{4.14}$$

$$C_\mu{}^{(k)} = \frac{(2k+1)(2J+1)C(21k;0\mu)(\gamma_1 L\|Y_2\|\gamma_1 L)(\gamma_2 S\|\mathbf{s}\|\gamma_2 A)\begin{Bmatrix} J & J & k \\ L & L & 2 \\ S & S & 1 \end{Bmatrix}}{(J\|\mathcal{G}_k\|J)}, \tag{4.15}$$

$$D^{(k)} = \frac{-(g-1)(2k+1)(2J+1)(\gamma_1 L\|Y_2\|\gamma_1 L)(\gamma_2 S\|\mathbf{s}\|\gamma_2 S)\begin{Bmatrix} J & J & k \\ L & L & 2 \\ S & S & 1 \end{Bmatrix}}{n(5)^{1/2}(J\|\mathcal{G}_k\|J)}. \tag{4.16}$$

The curly brackets in (4.14) and (4.15) [and (4.16)] are the usual 6-j and 9-j symbols, respectively. The quantities with double bars are submatrix elements (or reduced matrix elements) defined by the Wigner-Eckart theorem,

$$(\gamma'j'm'|T_{LM}|\gamma jm)$$
$$= (-)^{j'-m'}\begin{pmatrix} j'Lj \\ -m'Mm \end{pmatrix}(\gamma'j'\|T_L\|\gamma j), \tag{4.17}$$

where $\begin{pmatrix} j_1 j_2 j \\ m_1 m_2 m \end{pmatrix}$ is the so-called 3-j symbol of Wigner.[33]

All relevant submatrix elements are listed in Table III.

TABLE III. Submatrix elements, $n\leq 7$, $l=3$.

Submatrix element	Value
$(J\|\mathcal{G}_1\|J)$	$[J(J+1)(2J+1)]^{1/2}$
$(J\|\mathcal{G}_2\|J)$	$(1/2\sqrt{6})[(2J-1)2J(2J+1)(2J+2)(2J+3)]^{1/2}$
$(J\|\mathcal{G}_3\|J)$	$(1/4\sqrt{10})[(2J-2)(2J-1)\cdots(2J+4)]^{1/2}$
$(\gamma_2 S\|\mathbf{s}\|\gamma_2 S)$	$(1/n)[S(S+1)(2S+1)]^{1/2}$
$(\gamma_1 L\|Y_2\|\gamma_1 L)$	$\dfrac{-(7-n)(7-2n)[5(2L+3)(2L+2)(2L+1)]^{1/2}}{180[\pi(2L-1)2L]^{1/2}}$

[33] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959), Chap. 15.
[34] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), Chap. 7.

The submatrix elements of $\mathcal{G}_k$ and $\mathbf{s}(1)$ are trivial to obtain, given Table I and formulas for the 3-j symbols.[34,35] The submatrix element $(\gamma_1 L\|Y_2\|\gamma_1 L)$ is computed as follows: For $n\leq 2l+1$ and maximum S, the state of maximum L and M_L must, by the exclusion principle, have an angular part

$$|\gamma_1 LM_L=L\rangle = \mathfrak{A}Y_{ll}(1)Y_{ll-1}(2)\cdots Y_{l,l+1-N}(n), \tag{4.18}$$

where $\mathfrak{A}$ is the antisymmetrizing operator. Using (4.17), we have

$$(\gamma_1 LM_L=L|Y_{20}(1)|\gamma_1 LM_L=L)$$
$$=\begin{pmatrix} L & 2 & L \\ -L & 0 & L \end{pmatrix}(\gamma_1 L\|Y_2\|\gamma_1 L). \tag{4.19}$$

Given (4.18), the left-hand side is easily seen to be

$$\frac{1}{n}\sum_{m=l+1-n}\int Y_{l,-m}{}^*Y_{20}Y_{lm}d\Omega = \frac{1}{n}\begin{pmatrix} l & 2 & l \\ 0 & 0 & 0 \end{pmatrix}(2l+1)\frac{5}{4\pi}$$
$$\times \sum_{m=l+1-n}^{l}\begin{pmatrix} l & 2 & l \\ -m & 0 & m \end{pmatrix}. \tag{4.20}$$

[35] D. L. Falkoff, G. S. Colladay, and R. E. Sells, Can. J. Phys. **30**, 253 (1952).

TABLE IV. 9-j symbols.

Ion	State	$\begin{Bmatrix} J & J & 1 \\ L & L & 2 \\ S & S & 1 \end{Bmatrix}$	$\begin{Bmatrix} J & J & 3 \\ L & L & 2 \\ S & S & 1 \end{Bmatrix}$
Ce³⁺	$^2F_{5/2}$	$(2)^{1/2}/3\times7(5)^{1/2}$	$-1/7(2\times3\times5\times7)^{1/2}$
Pr³⁺	$^3H_4$	$2(2\times13)^{1/2}/3^2\times5(3\times5\times11)^{1/2}$	$-(2\times13)^{1/2}/3\times5\times11(3\times5)^{1/2}$
Nd³⁺	$^4I_{9/2}$	$3(7)^{1/2}/2\times5\times11(2\times13)^{1/2}$	$-3(3\times7)^{1/2}/2\times5\times11\times13(2)^{1/2}$
Pm³⁺	$^5I_4$	$2(2\times7)^{1/2}/3^2\times5(11\times13)^{1/2}$	$-(2\times7)^{1/2}/3\times5\times11(13)^{1/2}$
Sm³⁺	$^6H_{5/2}$	$(13)^{1/2}/3^2\times7(11)^{1/2}$	$-(13)^{1/2}/2\times3\times7(3\times7\times11)^{1/2}$
Eu³⁺	$^7F_0$	0	0
Gd³⁺	^8S	0	0
Tb³⁺	$^7F_6$	$-1/2^2\times3(7\times13)^{1/2}$	$(3)^{1/2}/2\times7(11\times13)^{1/2}$
Dy³⁺	$^6H_{15/2}$	$-(17)^{1/2}/2^2\times3(2\times7\times11\times13)^{1/2}$	$3(17\times19)^{1/2}/2^3\times7\times13(7\times11)^{1/2}$
Ho³⁺	$^5I_8$	$-(11)^{1/2}/5(5\times7\times13\times17)^{1/2}$	$(3\times11\times19)^{1/2}/5\times7(5\times7\times13\times17)^{1/2}$
Er³⁺	$^4I_{15/2}$	$-(11\times17)^{1/2}/2^2\times5^2(3\times7\times13)^{1/2}$	$3(3\times11\times17\times19)^{1/2}/2^2\times5^2\times7\times13(2\times7)^{1/2}$
Tm³⁺	$^3H_6$	$-(7)^{1/2}/2\times3\times13(11)^{1/2}$	$(3)^{1/2}/11\times13$
Yb³⁺	$^2F_{7/2}$	$-1/2^2\times7(2\times3)^{1/2}$	$(11)^{1/2}/2^3\times7(7)^{1/2}$

Standard formulas[38] for the 3-j symbols involved give

$$(\gamma_1 LM_L = L \,|\, Y_{20}(1) \,|\, \gamma_1 LM_L = L)$$

$$= -\left(\frac{5}{4\pi}\right)^{1/2} \frac{3S(l,n) - nl(l+1)}{n(2l+3)(2l-1)}, \quad (4.21)$$

where

$$S(l,n) = \sum_{l+1-n}^{l} m^2. \quad (4.22)$$

For the f shell, $l=3$ and the above formulas imply, for $n\leq7$,

$$(\gamma_1 L \| Y_2(1) \| \gamma_1 L) = \frac{-(7-n)(7-2n)(5)^{1/2}}{90\begin{pmatrix} L & 2 & L \\ -L & 0 & L \end{pmatrix}(4\pi)^{1/2}} \quad (4.23)$$

as given in Table III, after substituting for the 3-j symbol in (4.23). This completes the discussion of the submatrix elements.

Numerical values of the 9-j symbols for the appropriate values of L, S, J, and k do not in general seem to be available. They were therefore computed for all ground-state values of L, S, J of the partially filled $4f$ shell, for $k=1$ and 3, and are tabulated in Table IV.

The convenient formulas

$$5\begin{Bmatrix} 2 & L & L \\ L & 1 & 1 \end{Bmatrix}\begin{Bmatrix} J & J & 1 \\ L & L & 2 \\ S & S & 1 \end{Bmatrix} = \begin{Bmatrix} S & L & J \\ L & S & 1 \end{Bmatrix}\begin{Bmatrix} J & L & S \\ L & J & 1 \end{Bmatrix}$$

$$- \frac{(-)^{S+L+J}}{3(2L+1)}\begin{Bmatrix} S & J & L \\ J & S & 1 \end{Bmatrix}, \quad (4.24a)$$

$$7\begin{Bmatrix} J & J & 3 \\ 2 & 1 & J \end{Bmatrix}\begin{Bmatrix} J & J & 3 \\ L & L & 2 \\ S & S & 1 \end{Bmatrix} = (-)^{2J}\begin{Bmatrix} L & L & 2 \\ J & J & S \end{Bmatrix}\begin{Bmatrix} S & S & 1 \\ J & J & L \end{Bmatrix}$$

$$- 3\begin{Bmatrix} J & J & 1 \\ 2 & 1 & J \end{Bmatrix}\begin{Bmatrix} J & J & 1 \\ L & L & 2 \\ S & S & 1 \end{Bmatrix}, \quad (4.24b)$$

were used with tables[36] of 6-j symbols for the computation. The 9-j symbol $\begin{Bmatrix} J & J & j \\ L & L & l \\ S & S & s \end{Bmatrix}$ vanishes by reason of parity for $j+l+s=$ odd, accounting for the lack of a rank-2 tensor on the right side of (4.5) [see (4.15)]. This is the parity consideration alluded to earlier.

We now give formulas for the remaining quantities needed so that A and $C_\mu^{(k)}$ can be computed entirely by formulas contained in this Appendix.

$$\begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix} = 2(-)^{L+J+S}\frac{3X(X-1) - 4L(L+1)J(J+1)}{[(2L-1)2L(2L+1)(2L+2)(2L+3)\cdot(2J-1)2J(2J+1)(2J+2)(2J+3)]^{1/2}}, \quad (4.25)$$

where

$$X = J(J+1) + L(L+1) - S(S+1).$$

Also,

$$C(211; 0\mu) = (3\mu^2 - 2)/(10)^{1/2}, \quad (4.26a)$$

$$C(213; 0\mu) = [(3-\mu^2)/5]^{1/2}. \quad (4.26b)$$

We complete this Appendix by giving the results for $n>2l+1$. Let $n^*=4l+2-n$ be the number of holes. Also let $\psi(1\cdots n)\sim\bar\psi(1\cdots n^*)$ be the usual correspond-

[36] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., The 3-j and 6-j Symbols (Technology Press, Cambridge, Massachusetts, 1960).

ence[22] between states of the two configurations l^n and l^{n*}. It is not difficult to show[37] that

$$(\psi_f | \sum_{i=1}^{n} X_i | \psi_g) = (\Psi | \sum_{i=1}^{4l+2} X_i | \Psi) \delta_{fg}$$
$$+ (-)^{1+k+p} (\bar{\psi}_f | \sum_{i+1}^{n*} X_i | \bar{\psi}_g). \quad (4.27)$$

Here the operator X_i is of the type

$$X_i = R_{k\mu}(i) S_{p\nu}(i), \quad (4.28)$$

where $\mathbf{R}_k$ is a tensor of rank k operating on the spatial coordinates of particle i and $\mathbf{S}_p$ is of rank p acting on the spin ($p=0$, 1 for spin-$\frac{1}{2}$ particles). The symbol Ψ

[37] G. Racah, Phys. Rev. **62**, 438 (1942).

stands for a filled shell. Hence, the first term on the right of (4.27) is zero unless both k and p are zero. It follows from the preceding that, for $n \geq 2l+1$,

$$Y_{20}{}^{a}(1) \equiv - (n^*/n) A(n^*) g_{20}{}^{a}, \quad (4.29)$$

$$Y_{20}{}^{a}(1) s_{\mu}{}^{a}(1) \equiv + (n^*/n)[C_{\mu}{}^{(1)}(n^*) J_{\mu}{}^{a} + C_{\mu}{}^{(3)}(n^*) g_{3\mu}{}^{a}], \quad (4.30)$$

$$Y_{20}{}^{a}(1) s^{a}(1) \cdot s^{b}(1) \equiv (n^*/n)^2 [D^{(1)}(n^*) g_{20}{}^{ab} + D^{(3)}(n^*) G_{20}{}^{ab}]. \quad (4.31)$$

In (4.29), (4.30), and (4.31) we have indicated explicitly the dependence of the multiplying factors on the number of electrons. It enters into these factors via the submatrix elements of $Y_2(1)$ and $s_\mu(1)$ [also, via the factor $1/n$ in (4.16)].

Potential and Kinetic Electron Ejection from Molybdenum by Argon Ions and Neutral Atoms

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The yield of secondary electrons γ_n, from cleaned surfaces of polycrystalline molybdenum has been measured for argon neutral atoms (Ar^0) in the energy range 500–2500 eV. The values of γ_n thus obtained are compared with γ_i, the yield for argon ions previously determined. It is found that the rates of increase of γ_i and γ_n with energy E are not equal in the region of kinetic ejection. The ratio $(d\gamma_i/dE)/(d\gamma_n/dE)$ is 1.5. The result indicates that assumed models concerning the respective contributions of potential and kinetic ejection to the secondary electron yield at energies above 1000 eV should be modified.

THERE is a small amount of data available on the secondary electron yields, γ_n, resulting from neutral atom bombardment on well-defined surfaces.[1,2] We report here the measurement of γ_n for Ar^0 on clean Mo surface in the energy range 500–2500 eV and its comparison with the secondary electron yield, γ_i, for ions of argon previously reported.[3] Our results and their interpretation differ from those of Arifov *et al.*[2] who have recently reported measurements of the Ar^+, Ar^0 on Mo system.

The apparatus utilized for the measurement of the neutral beam flux in the target chamber is shown in Fig. 1. Fast neutral argon atoms are produced by charge transfer of argon ions in argon gas. The neutral flux at the target is between 10–30% of the ion beam at the same energy. The neutral beam flux is measured directly by a movable thermocouple probe (P) which has been previously calibrated by the ion beam. Output

of the probe is typically 250 μV/mW of beam power. In this calibration, it is assumed that the energy transfer coefficients for ions and neutrals of the same species at a given energy are identical. The detailed probe design and operation are to be reported separately. The surface cleaning of the Mo target and determination of monolayer formation time have been described previously.[3]
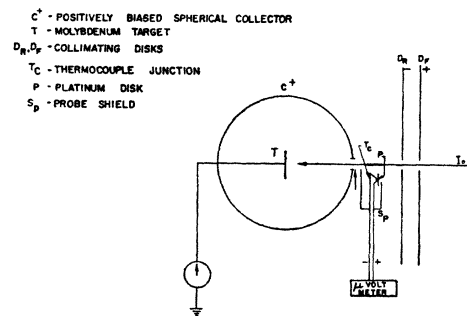

c⁺ - POSITIVELY BIASED SPHERICAL COLLECTOR
T - MOLYBDENUM TARGET
D_R, D_F - COLLIMATING DISKS
T_C - THERMOCOUPLE JUNCTION
P - PLATINUM DISK
S_p - PROBE SHIELD

FIG. 1. Schematic of target-collector-movable probe system.

[1] H. W. Berry; J. Appl. Phys. **29**, 1219 (1958).
[2] U. A. Arifov, R. R. Rakhimov, and Kh. Dzhurakulov; Soviet Phys.—Doklady **7**, 209 (1962).
[3] P. Mahadevan, J. K. Layton, and D. B. Medved, Phys. Rev. (to be published).