

## Indirect Exchange Coupling of Magnetic Moments in Rare-Earth Metals

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The Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism is examined for its relevance to ferromagnetism in the rare-earth metals. More specifically, the experimental sensitivity of the exchange energy (or Curie temperature) to the interatomic spacing (applied pressure) of the rare earths is examined in terms of the RKKY interaction. The form in which the interaction is usually examined, i.e., with the coupling parameter  $J(r)$  given by a Dirac  $\delta$  function, is unable to provide the observed sensitivity of Curie temperature to interatomic spacing. When this coupling parameter, or exchange interaction, is calculated with free-ion wave functions for the  $4f$  electrons, instead of the  $\delta$ -function approximation, agreement between theory and experiment is still not obtained. In this article, a modification of the coupling parameter is proposed which effectively takes into account some contribution of the crystal in determining the wave functions to be associated with the isolated magnetic moments. The procedure is phenomenological. Both the correct shape of the Curie-temperature-pressure curve and the sensitivity of the Curie temperature to pressure are obtained. Also the correct interlayer turn angle of the various elements is obtained. Undetermined multiplicative parameters appear in the final result which can be adjusted at some point in order to make the agreement quantitative. The conclusion is that the present modification of the RKKY interaction appears to account correctly for the origin of ferromagnetism in the rare-earth metals.

### I. INTRODUCTION

Several experiments have been performed<sup>1-5</sup> for the explicit purpose of determining the role of interatomic spacing in the origin of ferromagnetism in the rare-earth metals. The procedure is to determine experimentally the effect of pressure on the Curie temperature. Since the Curie temperature can be related to the magnetic interaction energy and the interatomic spacings can be related to the pressure, one can obtain an experimental connection between magnetic interaction energy and interatomic spacing. It is presently accepted that the Ruderman-Kittel-Kasuya-Yosida (RKKY)<sup>6-8</sup> exchange mechanism is responsible for ferromagnetism in the rare earths. Applications of the RKKY mechanism so far have fallen short, in a quantitative fashion, of accounting for the sensitivity of the Curie temperature to pressure that is observed experimentally and of explaining quantitatively the variation of the interlayer turn angle among the rare-earth elements.

It is the purpose of this article to examine the RKKY mechanism in some detail, first in order to determine specifically the origin of its shortcomings (as far as the applications are concerned), and second, to see to what extent corrections can be made. General familiarity with the theory will be assumed, and only a brief review will now be given

as a means of providing a source for specific references when modifications are made.

### II. RKKY INTERACTION

Ruderman and Kittel<sup>6</sup> accounted for the interaction between two nuclear spins  $\hat{I}_n$  and  $\hat{I}_m$  in terms of second-order perturbation theory in the following manner. The exchange energy  $H''(\vec{R})$  is given by

$$H''(\vec{R}) = \sum_{\vec{k}} \sum_{\vec{k}'} \sum_s \sum_{s'} \frac{\langle \vec{k}s | \mathcal{H} | \vec{k}'s' \rangle \langle \vec{k}'s' | \mathcal{H} | \vec{k}s \rangle}{E_k - E_{k'}}, \quad (1)$$

where all symbols have their usual meaning and  $\vec{R} = \vec{R}_m - \vec{R}_n$  is the internuclear distance. In Eq. (1),

$$\begin{aligned} \mathcal{H} = & \frac{1}{2} \sum_{\vec{k}} \sum_{\vec{k}'} e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_n} J(\vec{k}', \vec{k}) [I_n^+ C_{\vec{k}}^{\dagger}, C_{\vec{k}'} \\ & + I_n^- C_{\vec{k}}^{\dagger}, C_{\vec{k}'} + I_n^x (C_{\vec{k}}^{\dagger}, C_{\vec{k}'} - C_{\vec{k}'}^{\dagger}, C_{\vec{k}})], \end{aligned} \quad (2)$$

where the  $C_{\vec{k}}^{\dagger}$ ,  $C_{\vec{k}}$ , etc., are creation and annihilation operators. In general,

$$J(\vec{k}', \vec{k}) = \int d^3r \phi_{\vec{k}'}^*(\vec{r}) \alpha(r) \phi_{\vec{k}}(\vec{r}), \quad (3)$$

whereas for the nuclear-spin case,

$$\alpha(r) = J_0 \delta(r), \quad (4)$$

and hence

$$J(\vec{k}', \vec{k}) = J_0. \quad (5)$$

Utilizing Eqs. (2) and (5), one finds the following

form for Eq. (1), viz.:

$$H''(\vec{R}) = J_0^2 \sum_{\vec{k}} \sum_{\vec{k}'} \frac{\exp[-i(\vec{k} - \vec{k}') \cdot (\vec{R}_m - \vec{R}_n)]}{E_{\vec{k}} - E_{\vec{k}'}} \times \sum_s \langle s | (\vec{S} \cdot \vec{I}_m)(\vec{S} \cdot \vec{I}_n) | s \rangle. \quad (6)$$

Replacing the sums in Eq. (6) by integrals and paying proper attention to the current ranges of  $\vec{k}$  and  $\vec{k}'$  gives

$$H''(\vec{R}) = \frac{J_0^2}{2} (\vec{I}_m \cdot \vec{I}_n) \frac{2m^*}{(2\pi)^6} \int_0^{k_F} d^3k e^{-i\vec{k} \cdot \vec{R}} \times \int_0^\infty d^3k' \frac{e^{i\vec{k}' \cdot \vec{R}}}{k^2 - (k')^2}. \quad (7)$$

The final form for Eq. (7) is

$$H''(\vec{R}) = [4J_0^2 m^* k_F^4 / (2\pi)^3] (\vec{I}_m \cdot \vec{I}_n) \Phi(2k_F R), \quad (8)$$

where

$$\Phi(x) = [(x \cos x - \sin x)/x^4]. \quad (9)$$

Kasuya<sup>7</sup> and Yosida<sup>8</sup> assumed that ferromagnetism in the rare earths could be explained by essentially the same type of relationship as that given in Eq. (8), except that the parameter  $J_0$  is replaced by an exchange integral as in Eq. (3), in which some dependence on  $\vec{k}$  and  $\vec{k}'$  is retained.  $H''(\vec{R})$  in Eq. (8), has been calculated with various approximations for  $J(\vec{k}, \vec{k}')$ , replacing  $J_0$ .

Elliott<sup>9</sup> stated that this exchange interaction  $J(\vec{k}', \vec{k})$  between a conduction electron and a  $4f$  electron is similar to the atomic  $6s-4f$  and also  $5d-4f$  exchange integrals. We note that when a conduction electron is in the vicinity of a rare-earth ion, this free electron looks like one of the  $6s$  or  $5d$  electrons to the rare-earth ion (which it has lost to the conduction band). Elliott also asserts that  $J(\vec{k}', \vec{k})$  probably will not depend strongly on  $\vec{k}$  or  $\vec{k}'$ .

van der Braak and Caspers<sup>10</sup> calculated  $J(\vec{k}', \vec{k})$  by using  $4f$  wave functions given by Freeman and Watson<sup>11</sup> and with free-electron wave functions for the conduction electron. The exchange integral  $J''(\vec{R})$  of Eq. (1) or (8) is very insensitive, in this approximation, to interatomic spacing (contrary to experiment).

Milstein and Robinson<sup>12</sup> improved the calculation of  $J(\vec{k}', \vec{k})$  by using a  $6s$ -electron wave function (rather than a plane wave as had been used by van der Braak and Caspers). Again the source of both the  $4f$  and  $6s$  wave functions was Freeman and Watson.<sup>11</sup> Again, the  $H''(\vec{R})$  so calculated is quite insensitive to interatomic spacing.

### III. SPECIAL MODIFICATION

We now make a special modification of the procedure of calculation which has been used up to now. We do not assume that  $J(\vec{k}', \vec{k})$  is independent

of both  $\vec{k}'$  and  $\vec{k}$ . In order to see the qualitative effects of  $\vec{k}'$  and  $\vec{k}$ , we choose a special form for  $J(\vec{k}', \vec{k})$  to go into Eq. (2). The bases of the choice are twofold: (a)  $J(\vec{k}', \vec{k})$  must be amenable to analysis so that closed-form results can be obtained, and (b) it must have some relationship to reality (physics). We now proceed with the construction of a  $J(\vec{k}', \vec{k})$  satisfying these two objectives.

To extend the result for the nuclear-spin case that we obtained by following a procedure similar to that of Kittel to the indirect exchange coupling of magnetic ions in the rare-earth metals [Eq. (8)], we use the exchange interaction instead of the contact hyperfine interaction. We can start with the Heisenberg Hamiltonian,

$$\mathcal{H} = -2J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (10)$$

and proceed as we did with the hyperfine interaction Hamiltonian and obtain

$$H = -\frac{1}{N} \sum_{\vec{k}} \sum_{\vec{k}'} \sum_n e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_n} J(\vec{k}, \vec{k}') \times [I_n^* C_{\vec{k}'}^\dagger, C_{\vec{k}}^\dagger + I_n^- C_{\vec{k}'}^\dagger, C_{\vec{k}}^\dagger + I_n^z (C_{\vec{k}'}^\dagger, C_{\vec{k}}^\dagger - C_{\vec{k}'}^\dagger, C_{\vec{k}}^\dagger)], \quad (11)$$

where  $N$  is the total number of magnetic lattice points in a unit volume and  $J(\vec{k}', \vec{k})$  is the exchange integral between a conduction electron and the  $f$ -core spin of the magnetic ion. It has been traditional to assume the exchange coupling to be a function only of  $q = |\vec{k}' - \vec{k}|$ , i. e., to set  $J(\vec{k}', \vec{k}) = J(q)$ , yielding a  $J$  which is effectively the Fourier transform of some quantity.<sup>13</sup> The exchange integral may be written

$$J(\vec{k}', \vec{k}) = \int \int N \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] \phi_{\vec{k}'}^*(\vec{r}_1) \times \phi_{4f}^*(\vec{r}_2) e^2 \phi_{\vec{k}}(\vec{r}_2) \phi_{4f}(\vec{r}_1) d^3r_1 d^3r_2 / r_{12} \quad (12)$$

and it does not depend on the lattice position  $R_n$ .

The bare Coulomb interaction gives an infinitely large interaction between plane waves in the limit of vanishing momentum transfer ( $\vec{k} - \vec{k}' \rightarrow 0$ ). This implies an extremely strong long-range interaction. Since the exchange interaction in the rare earths is a short-range interaction, strong shielding, within an atomic volume, of the conduction electron-local moment interaction can be assumed. A simplification which depends on this electron-electron screening for justification results from approximating the Coulomb interaction  $e^2/r_{12}$  by the  $\delta$  function  $-\delta(r_1 - r_2)$ .<sup>14-18</sup> Therefore, replacing the Coulomb interaction by this isotropically screened interaction, we get

$$J(q) = N e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_n} \int e^{i\vec{q} \cdot \vec{r}} |\phi_{4f}(\vec{r})|^2 d^3r, \quad (13)$$

where  $\vec{q} = \vec{k} - \vec{k}'$ . We see that the exchange-scatter-

ing matrix elements reduce to magnetic form factors for short-range interactions. The constants in front of the integral in Eq. (13) cancel with those in Eq. (11), leaving

$$J(q) = \int e^{i\vec{q}\cdot\vec{r}} |\phi_{4f}(\vec{r})|^2 d^3r. \quad (14)$$

It is possible to expand the  $4f$  wave functions as

$$\phi_{4f}(\vec{r}) = R_{4f} \sum_{m=-3}^3 Y_l^m(\theta, \varphi), \quad (15)$$

where  $R_{4f}(r)$  is the radial wave function and  $Y_l^m(\theta, \varphi)$  are spherical harmonics (Kaplan and Lyons<sup>19</sup> and later Specht<sup>20</sup> have made calculations on the general form of the nonisotropic terms of the interaction). Freeman and Watson<sup>11</sup> have made Hartree-Fock calculations for a free ion to obtain the radial wave functions. The  $4f$  function for  $Gd^{+3}$  was given in the form

$$rR_{4f}(r) = \sum_{i=1}^4 C_i r^4 e^{-\alpha_i r}. \quad (16)$$

If we substitute this expression for the  $4f$  wave function into Eq. (14) and evaluate the integral, we get

$$\begin{aligned} J(q) &= 2\pi \int_0^\infty |\phi_{4f}(r)|^2 r^2 dr \int_0^\pi e^{iqr \cos\theta} \sin\theta d\theta \\ &= 4\pi \int_0^\infty |rR_{4f}(r)|^2 (\sin qr / qr) dr \\ &= (4\pi/q) \int_0^\infty r^2 F(r) \sin qr dr, \end{aligned} \quad (17)$$

where  $F(r)$  has the form  $Ce^{-Zr}$ . Continuing, we get

$$J(q) \sim cq^{-9}. \quad (18)$$

This expression introduces an integral with eighteenth-order poles into the second-order interaction. We can use the computer to evaluate the remaining integrals, or we can try an approximating technique, since we are only interested in examining the general feasibility of including the atomic dimensions of the  $4f$  wave functions.

Our procedure is to choose a function for  $J(q)$  that can be integrated and then to use Fourier-transform theory to find the corresponding function that represents the  $4f$  wave function. The chosen function must satisfy our two stated objectives. From Eq. (14), we observe that  $J(q)$  and  $|\phi_{4f}(r)|^2$  are Fourier-transform pairs. From here on, we denote this approximate  $|\phi_{4f}(r)|^2$  by  $F(r)$ . Thus, after postulating a trial function  $J(q)$  we can take its Fourier transform to find  $F(r)$ , or vice versa.

Our procedure is a significant departure from the usual discussions in the following way. Instead of using the free-ion wave functions like those computed by Freeman and Watson, we propose to use wave functions of the form

$$\phi_{4f}(\text{crystal}) = \sum_n a_n \mathcal{B}_n(\beta, r) Q(q_0, r) + iG(\beta, q_0, r), \quad (19)$$

where the  $Q_n(q_0, r)$  are functions depending only on properties of the free-ion functions and the  $\mathcal{B}_n(\beta, r)$  depend only on properties of the lattice.  $G(\beta, q_0, r)$  depends on the properties of both the lattice and the free-ion function. There are several possible formal procedures whereby the functions and coefficients  $a_n$  can be calculated. In this present article, we do not attempt to select the "best possible"  $\phi_{4f}(\text{crystal})$  but rather to utilize simple functions which will yield closed form results.

We choose as our trial function

$$J(q) = Ae^{-\beta|q-q_0|}, \quad (20)$$

and notice the boundary conditions; as  $\beta \rightarrow 0$ , we have  $J$  equal to a constant, independent of  $k$  and  $k'$  as often assumed; and as  $\beta \rightarrow \infty$ , we have  $J$  equal to zero. Fourier-transform theory tells us that  $\beta$  and  $q_0$  in  $J(q)$  are related to the width and shape of the  $4f$  wave function.

Now we can use this  $J(q)$  to calculate the second-order interaction of the magnetic ions. Starting with Eq. (1), one finds

$$H''(\vec{R}) = \sum_{\mathbf{k}}' \sum_{\mathbf{k}'}' \sum_{\mathbf{s}}' \sum_{\mathbf{s}'}' \frac{\langle \mathbf{k} \mathbf{s} | \mathcal{H} | \mathbf{k}' \mathbf{s}' \rangle \langle \mathbf{k}' \mathbf{s}' | \mathcal{H} | \mathbf{k} \mathbf{s} \rangle}{E_{\mathbf{k}} - E_{\mathbf{k}'}}; \quad (21)$$

we have

$$\begin{aligned} \langle \mathbf{k}' \mathbf{s}' | \mathcal{H} | \mathbf{k} \mathbf{s} \rangle &= \sum_{\substack{\mathbf{k} \\ \mathbf{s} \\ \mathbf{s}'}}' e^{i(\vec{k}-\vec{k}')\cdot\vec{R}} J(q) \langle \mathbf{s}' | \vec{\mathbf{s}} \cdot \vec{\mathbf{I}}_{\mathbf{n}} | \mathbf{s} \rangle \\ &\quad \times C_{\mathbf{k}'\mathbf{s}'}^{\dagger} C_{\mathbf{k}\mathbf{s}}, \end{aligned} \quad (22a)$$

and

$$\begin{aligned} \langle \mathbf{k} \mathbf{s} | \mathcal{H} | \mathbf{k}' \mathbf{s}' \rangle &= \sum_{\substack{\mathbf{k} \\ \mathbf{s} \\ \mathbf{s}'}}' e^{i(\vec{k}'-\vec{k})\cdot\vec{R}} J(q) \langle \mathbf{s} | \vec{\mathbf{s}} \cdot \vec{\mathbf{I}}_{\mathbf{n}} | \mathbf{s}' \rangle \\ &\quad \times C_{\mathbf{k}\mathbf{s}}^{\dagger} C_{\mathbf{k}'\mathbf{s}'}, \end{aligned} \quad (22b)$$

with  $J(q)$  as given in Eq. (20). The summations extend over all values of  $\mathbf{k}$  and  $\mathbf{k}'$ , so if we change  $\vec{k}$  to  $-\vec{k}$  and  $\vec{k}'$  to  $-\vec{k}'$  in the summations, we get

$$\sum_{\vec{k}}' \sum_{\vec{k}'}' - \frac{1}{2} \left( \sum_{\vec{k}}' \sum_{\vec{k}'}' + \sum_{-\vec{k}}' \sum_{-\vec{k}'}' \right). \quad (23)$$

Since  $e^{i\mathbf{k}\cdot\mathbf{r}} = (e^{-i\mathbf{k}\cdot\mathbf{r}})^*$ , this change has the effect of adding the complex-conjugate terms (c. c.) to the right-hand side of Eq. (21). Using Eq. (23) and performing a similar analysis as was done earlier, we obtain

$$\begin{aligned} H''(\vec{R}) &= \frac{1}{2} (\vec{\mathbf{s}}_{\mathbf{n}} \cdot \vec{\mathbf{s}}_{\mathbf{m}}) \frac{m^*}{(2\pi)^6} \int_0^{k_F} e^{-i\vec{k}\cdot\vec{R}} d^3k \\ &\quad \times \int_0^\infty \frac{|J(\vec{k}, \vec{k}')|^2 e^{i\vec{k}'\cdot\vec{R}} d^3k'}{k^2 - (k')^2} + \text{c. c.} \end{aligned} \quad (24)$$

Since  $\vec{k}' - \vec{k} = \vec{q}$  and the Jacobian is 1, we can change variables from  $\vec{k}, \vec{k}'$  to  $\vec{k}, \vec{q}$ :

$$H''(\vec{R}) = \frac{1}{2} (\vec{\mathbf{s}}_{\mathbf{n}} \cdot \vec{\mathbf{s}}_{\mathbf{m}}) \frac{m^*}{(2\pi)^6} \int_{-\infty}^\infty |J(q)|^2 e^{i\vec{q}\cdot\vec{R}} d^3q$$

$$\times \int_{-k_f}^{k_f} \frac{d^3 k}{k^2 - (k+q)^2} + c. c. \tag{25}$$

No physical significance can be attached to the negative values of  $k$  or  $q$  in Eq. (25), but it is a mathematical convenience to express the results in terms of paths which are symmetrical about the origin, as exponential rather than trigonometric functions that appear in the integrand.<sup>21</sup> The fact that the limits on the integrals appear as they do can be seen by changing  $k$  to  $-k$  and  $q$  to  $-q$  in the integrands.

We integrate first over  $\vec{k}$  space, holding  $\vec{q}$  constant. The  $\vec{k}$  integration is most easily done in cylindrical coordinates, with the  $z$  axis parallel to  $\vec{q}$ . We have

$$\begin{aligned} H''(\vec{R}) &= \frac{1}{2} \vec{S}_n \cdot \vec{S}_m \frac{m^*}{(2\pi)^6} \int_{-\infty}^{\infty} e^{i\vec{q} \cdot \vec{R}} |J(q)|^2 d^3 q \\ &\times \int_{-k_f}^{k_f} \frac{dk_z}{k^2 - (k^2 + q^2 + 2qk_z)} \int_0^{(k_f^2 - k_z^2)^{1/2}} k_r dk_r \\ &\times \int_0^{2\pi} dk_\phi + c. c. \\ &= -\pi \vec{S}_n \cdot \vec{S}_m \frac{m^*}{(2\pi)^6} \int e^{i\vec{q} \cdot \vec{R}} |J(q)|^2 f(q) d^3 q + c. c. , \end{aligned} \tag{26}$$

where

$$f(q) = \int_{-k_f}^{k_f} \frac{(k_f^2 - k_z^2)}{2k_z q + q^2} dk_z . \tag{27}$$

Evaluating  $f(q)$  is facilitated by breaking it up into two integrals,

$$f(q) = \int_{-k_f}^{k_f} \frac{k_f^2 dk_z}{2qk_z + q^2} - \int_{-k_f}^{k_f} \frac{k_z^2 dk_z}{2qk_z + q^2} . \tag{28}$$

Changing the variable of integration in the first integral to  $2qk_z + q^2$ , we obtain

$$f(q) = \int_{-2qk_f + q^2}^{2qk_f + q^2} \frac{k_f^2 dx}{2qx} - \int_{-k_f}^{k_f} \frac{k_z^2 dk_z}{2qk_z + q^2} . \tag{29}$$

Equation (29) becomes

$$f(q) = \frac{k_f}{2} + \frac{1}{2q} (k_f^2 - \frac{1}{4} q^2) \ln \left| \frac{q + 2k_f}{q - 2k_f} \right| . \tag{30}$$

After spherical coordinates are introduced and the angular integrations performed, Eq. (26) becomes

$$\begin{aligned} H''(\vec{R}) &= - (2\pi^2/iR) \vec{S}_n \cdot \vec{S}_m [m^*/(2\pi)^6] \\ &\times \int_{-\infty}^{\infty} q e^{iqR} f(q) A e^{-2\beta|q-a_0|} dq + c. c. \end{aligned} \tag{31}$$

This integral can be evaluated in terms of elementary functions by straightforward quadrature, but this procedure is somewhat tedious. However, this integration can be greatly simplified by an application of contour integration suggested by Van Vleck.<sup>21</sup> The integral is only infinitesimally changed if we deform the path to go infinitesimally above a cut along the axis extending from  $q = -2k_f$  to  $q = 2k_f$  in the complex  $q$  plane. If Eq. (30) had no absolute value signs, the integral would then be zero. This we can observe by completing the contour with an infinite semicircle in the upper-half of the complex  $q$  plane; the resulting contour encloses no singularities since with the slightly deformed path the branch points of the logarithm are avoided, and there is no contribution from the infinite arc since  $qf(q)$  vanishes like  $1/q$  for large  $|q|$ . Thus, subtracting the integral with the absolute value sign removed from the argument of the logarithm in the integral as it stands yields the integral in Eq. (31). Then the imaginary part of the logarithm is  $\pi i$  for the part of the path just above the cut.<sup>21</sup> That is,

$$\ln \left( \frac{q + 2k_f}{q - 2k_f} \right) = \ln \left| \frac{q + 2k_f}{q - 2k_f} \right| + \pi i .$$

Thus, we arrive at the relation

$$\begin{aligned} H''(\vec{R}) &= - (2\pi^2/iR) \vec{S}_n \cdot \vec{S}_m [m^* A^2 / (2\pi)^6] \\ &\times \int_{-\infty}^{\infty} dq e^{iqR} e^{-2\beta|q-a_0|} \frac{1}{2} (k_f^2 - \frac{1}{4} q^2) \\ &\times \left[ \ln \left| \frac{q + 2k_f}{q - 2k_f} \right| - \ln \left( \frac{q + 2k_f}{q - 2k_f} \right) \right] + c. c. \\ &= - (\pi^2/iR) \vec{S}_n \cdot \vec{S}_m [m^* A^2 / (2\pi)^6] \\ &\times \int_{-2k_f}^{2k_f} e^{iqR} dq e^{-2\beta|q-a_0|} (k_f - \frac{1}{4} q^2) (-\pi i) + c. c. \end{aligned} \tag{32}$$

Breaking up the integral into  $\int_{-2k_f}^{q_0}$  and  $\int_{q_0}^{2k_f}$ , we may remove the absolute value signs from the integrand and the integration is performed. The coefficient of  $\vec{S}_n \cdot \vec{S}_m$  may be regarded as an effective exchange interaction, i. e.,  $-2\mathcal{J}(\vec{R})$ ,

$$\begin{aligned} \mathcal{J}(R) &= - [\pi^3 m^* A^2 / 2R (2\pi)^6] \left[ \int_{-2k_f}^{q_0} e^{iqR} e^{-2\beta(a_0-q)} \right. \\ &\times (k_f^2 - \frac{1}{4} q^2) dq \\ &\left. + \int_{q_0}^{2k_f} e^{iqR} e^{-2\beta(a_0-q)} (k_f^2 - \frac{1}{4} q^2) dq \right] + c. c. \end{aligned} \tag{33}$$

Performing the indicated integrations in Eq. (33) yields

$$\mathcal{J}(R) = \frac{A^2 m^*}{2^7 \pi^3} \left( \frac{4\beta e^{iq_0 R} (q_0^2 - 4k_f^2)}{R(R^2 + 4\beta^2)} + \frac{e^{-2\beta a_0}}{2R(R - i2\beta)^3} [q_0(R - i2\beta) \cos q_0(R - i2\beta) - \sin q_0(R - i2\beta)] \right)$$

$$\begin{aligned}
& - [e^{2\beta q_0}/2R(R+i2\beta)^3][q_0(R+i2\beta)\cos q_0(R+i2\beta) - \sin q_0(R+i2\beta)] \\
& + [e^{-2\beta q_0}/2R(R-i2\beta)^3][2k_f(R-i2\beta)\cos 2k_f(R-i2\beta) - \sin 2k_f(R-i2\beta)] \\
& + [e^{2\beta q_0}/2R(R+i2\beta)^3][2k_f(R+i2\beta)\cos 2k_f(R+i2\beta) - \sin 2k_f(R+i2\beta)] + \text{c. c.}
\end{aligned} \tag{34}$$

it is convenient to break the first part of the equation up into its real and imaginary terms. Then when we add this to its complex conjugate, we obtain a real expression. We know that for a Hermitian Hamiltonian, the energy must be real. Using the relation

$$\begin{aligned}
(x+iy)\cos(x+iy) - \sin(x+iy) &= x\cos x \cosh y + y\sin x \sinh y - \sin x \cosh y \\
&+ i(y\cos x \cosh y - x\sin x \sinh y - \cos x \sinh y)
\end{aligned}$$

and performing quite a bit of relatively simple algebra, we can obtain our final expression

$$\begin{aligned}
\mathcal{J}(R) &= \frac{m^*A^2}{2^6\pi^3} \left[ \frac{4\beta \cos q_0 R (q_0^2 - 4k_f^2)}{R(R^2 + 4\beta^2)} \right. \\
&- \left( \frac{e^{2\beta q_0} - e^{-2\beta q_0}}{2R} \right) \left( \frac{(R^3 - 12R\beta^2)(q_0 R \cos q_0 R \cosh 2q_0\beta + 2q_0\beta \sin q_0 R \sinh 2q_0\beta - \sin q_0 R \cosh 2q_0\beta)}{R^6 + 12R^4\beta^2 + 48R^2\beta^4 + 64\beta^6} \right) \\
&- \left( \frac{e^{2\beta q_0} - e^{-2\beta q_0}}{2R} \right) \left( \frac{(6R^2\beta - 8\beta^3)(2q_0\beta \cos q_0 R \cosh 2q_0\beta - q_0 R \sin q_0 R \sinh 2q_0\beta - \cos q_0 R \sinh 2q_0\beta)}{R^6 + 12R^4\beta^2 + 48R^2\beta^4 + 64\beta^6} \right) \\
&+ \left( \frac{e^{2\beta q_0} + e^{-2\beta q_0}}{2R} \right) \left( \frac{(R^3 - 12R\beta^2)(2k_f R \cos 2k_f R \cosh 4k_f\beta + 4k_f\beta \sin 2k_f R \sinh 4k_f\beta - \sin 2k_f R \cosh 4k_f\beta)}{R^6 + 12R^4\beta^2 + 48R^2\beta^4 + 64\beta^6} \right) \\
&+ \left. \left( \frac{e^{2\beta q_0} + e^{-2\beta q_0}}{2R} \right) \left( \frac{(6R^2\beta - 8\beta^3)(4k_f\beta \cos 2k_f R \cosh 4k_f\beta - 2k_f R \sin 2k_f R \sinh 4k_f\beta - \cos 2k_f R \sinh 4k_f\beta)}{R^6 + 12R^4\beta^2 + 48R^2\beta^4 + 64\beta^6} \right) \right]. \tag{35}
\end{aligned}$$

We note that this function exhibits the proper behavior at the boundaries, i. e., as  $\beta \rightarrow 0$ ,  $\mathcal{J}(R) \rightarrow \Phi(2k_f R)$ , and as  $\beta \rightarrow \infty$ ,  $\mathcal{J}(R) \rightarrow 0$ .

In our earlier discussion about the origin of  $J(q)$ , we said that the Fourier transform of  $J(q)$  must represent the  $4f$  radial wave function. Therefore, we must now find the Fourier transform of  $J(q)$ , which is  $F(r)$ .  $F(r)$  is defined as

$$F(r) = (2\pi)^{-3} \int e^{-i\vec{q} \cdot \vec{r}} A e^{-\beta|q-q_0|} d^3q. \tag{36}$$

The absolute value signs force us to break the integral up into two regions such that  $q - q_0$  is always positive, i. e.,

$$\begin{aligned}
F(r) &= [A/(2\pi)^3] \left[ \int_0^{q_0} e^{-i\vec{q} \cdot \vec{r}} e^{-\beta(q_0 - q)} d^3q \right. \\
&+ \left. \int_{q_0}^{\infty} e^{-i\vec{q} \cdot \vec{r}} e^{-\beta(q - q_0)} d^3q \right] \\
&= [A2\pi/(2\pi)^3] [e^{-\beta q_0} \int_0^{q_0} e^{\beta q} q^2 dq \int_{-1}^1 e^{-iqr} du \\
&+ e^{\beta q_0} \int_{q_0}^{\infty} e^{-\beta q} q^2 dq \int_{-1}^1 e^{-iqr} du] \\
&= (A/2\pi^2 r) [e^{-\beta q_0} \int_0^{q_0} q e^{\beta q} \sin qr dq \\
&+ e^{\beta q_0} \int_{q_0}^{\infty} q e^{-\beta q} \sin qr dq]. \tag{37}
\end{aligned}$$

We then obtain as  $F(r)$  the following expression:

$$F(r) = [A/r(\beta^2 + r^2)\pi^2] (q_0\beta \sin q_0 r$$

$$\begin{aligned}
&- \frac{1}{2} e^{-\beta q_0} \int_0^{q_0} e^{\beta q} (\beta \sin qr - r \cos qr) dq \\
&+ \frac{1}{2} e^{\beta q_0} \int_{q_0}^{\infty} e^{-\beta q} (\beta \sin qr + r \cos qr) dq \\
&= A \left( \frac{q_0\beta \sin q_0 r}{\pi^2 r(\beta^2 + r^2)} + \frac{\beta(2 \cos q_0 r - e^{-\beta q_0})}{\pi^2(\beta^2 + r^2)^2} \right), \tag{38}
\end{aligned}$$

which is the form required by Eq. (19). *The main aspect of what has been accomplished by this technique is that additional properties of the material, i. e.,  $\beta$ , have been introduced into the wave functions representing the magnetic moments of the ions.* In the past, free-ion wave functions have been used to represent the magnetic moments. This present procedure effectively modifies the free-ion wave functions in a phenomenological way. Studies are under way for the accomplishment of this modification in a more direct and mechanistic way.

The next step in this treatment is to ascertain appropriate values for  $A$ ,  $q_0$ , and  $\beta$ . There are several ways to pick the values such that these parameters let the Fourier transform of the test function  $J(q)$  accurately represent the  $4f$  radial wave function. It is proper to compare  $r^2 F(r)$  with  $|rR_{4f}(r)|^2$  since they both represent electron density distributions. One way would be to fit the first and second moments of the  $4f$  wave functions

to the first and second moments of  $r^2 F(r)$  and obtain two analytic equations which could be solved for  $\beta$  and  $q_0$ . This moment-fitting procedure would yield equations

$$\begin{aligned} \bar{r} &= \int_0^\infty r |rR_{4f}|^2 dr / \int_0^\infty |rR_{4f}|^2 dr \\ &= \int_0^\infty r^3 F(r) dr / \int_0^\infty r^2 F(r) dr \end{aligned} \quad (39)$$

and

$$\begin{aligned} \overline{(r^2)} &= \int_0^\infty r^2 |rR_{4f}|^2 dr / \int_0^\infty |rR_{4f}|^2 dr \\ &= \int_0^\infty r^4 F(r) dr / \int_0^\infty r^2 F(r) dr \end{aligned} \quad (40)$$

Of course, the  $4f$  radial wave functions are normalized over all space, so the denominators in the left-hand sides of Eqs. (39) and (40) are unity. The requirement that the  $F(r)$  function be normalized would yield the third parameter  $A$ , once  $\beta$  and  $q_0$  are found. Since

$$F(r) = (2\pi)^{-3} \int A e^{-\beta|q-r_0|} e^{-i\vec{q}\cdot\vec{r}} d^3q \quad (41)$$

and its inverse is

$$A e^{-\beta|q-r_0|} = \int e^{i\vec{q}\cdot\vec{r}} F(r) d^3r, \quad (42)$$

letting  $q=0$  gives

$$A e^{\beta q_0} = \int F(r) d^3r.$$

The requirement that  $F(r)$  be normalized thus yields

$$A e^{\beta q_0} = 1. \quad (43)$$

These techniques could give us analytic expressions which would yield exact values for  $A$ ,  $\beta$ , and  $q_0$ . However, these techniques are not satisfactory because the  $4f$  radial wave functions are normalized over all space, but  $F(r)$  has no meaning outside of the  $4f$  shell, and since it is oscillatory, fitting its moments to the moments of  $|rR_{4f}|^2$  would yield spurious results. And  $A$  would have to be found from the requirement that  $F(r)$  is normalized only out to the radial extent of the  $4f$  wave function.

Because of these limitations in the analytic technique, another method of finding  $\beta$ ,  $q_0$ , and  $A$  would be to select empirically the parameter values that give a good fit between the two curves.

#### IV. CONCLUSIONS

Now we can analyze the exchange interaction energy. We will use our expression for the exchange interaction energy Eq. (35) to investigate two pertinent aspects of the problem. The first aspect of this problem that we consider is the dependence of the magnetic transition temperature upon interatomic distance. The second is the dependence of interlayer turn angle upon properties of the crystal; this interlayer turn angle is formed by magnetic moments in successive atomic planes.

For simplicity we now use the first term approximation in investigating the first aspect

$$\mathcal{J}(R) = \frac{m^* A^2}{2^6 \pi^3} \frac{4\beta \cos q_0 R}{R(R^2 + 4\beta^2)} (q_0^2 - 4k_f^2). \quad (44)$$

Of course, we have already mentioned that when  $\beta \rightarrow 0$ , the only surviving terms in  $\mathcal{J}(R)$  are the parts of the third term that equal  $\Phi(2k_f R)$ , the familiar Ruderman-Kittel function.

The expression for the paramagnetic Curie temperature in terms of Eq. (44) is

$$k_B T_p = (g-1)^2 j(j+1) \frac{m^* A^2}{3\pi^3 2^6} (q_0^2 - 4k_f^2) \sum_R \frac{4\beta \cos q_0 R}{R(R^2 + 4\beta^2)}. \quad (45)$$

Since the molecular field theory does not distinguish between  $T_c$  and  $T_p$ , this equation will be used to represent both. Setting

$$C_1 = (m^* A^2 / 96 k_B \pi^3) (q_0^2 - 4k_f^2) \quad (46)$$

allows us to write Eq. (45) in the following convenient form:

$$\frac{T_p}{(g-1)^2 j(j+1) C_1} = \sum_R \frac{\cos q_0 R}{\beta R [1 + (R/2\beta)^2]}. \quad (47)$$

The experimental variations of the Curie temperature with interatomic spacing (pressure) can be correlated with parameters of the materials in several ways, two of which will now be discussed. In the first case,  $d/2r_f$  can be used as the materials parameter where  $d$  is the average interatomic distance and  $r_f$  is the radius of the  $4f$  electron orbital. Such an interaction curve was proposed by Milstein in his M.S. thesis and reported in Ref. 1. This curve is repeated here as our Fig. 1. In the second case, the  $c/a$  ratio of the hexagonal crystal can be used as the materials parameter, with which variations of the Curie temperature are correlated. Such an interaction curve was proposed by Milstein in his Ph.D. thesis and reported in Refs. 4 and 5. Since both parameters  $d/2r_f$  and  $c/a$  give essentially the same type of correlation with  $T_c$ , it would appear that there exists some relationship between the parameters themselves.

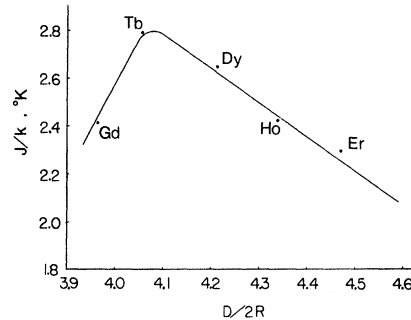


FIG. 1. Exchange-interaction curve for the ferromagnetic rare-earth metals (Ref. 1).

In the case of the first type of interaction curve, no theoretical justification exists in the RKKY theory for the role of the  $d/2r_f$  parameter. In the case of the second type of interaction curve, the Ruderman-Kittel function  $\Phi(2k_F R)$  can be written as a unique function of  $(c/a)$ , viz.,  $\Phi(c/a)$ . As part of the present study, this function was evaluated for several values of  $c/a$ ; however, the sensitivity of the Curie temperature to  $c/a$ , as determined experimentally, does not show up in the calculation. With this new modification made in this present article, the RKKY theory can show the sensitivity to a  $(d/2r_f)$ -like parameter that is obtained experimentally. We now proceed to make the proper identification of the parameters in Eq. (38) with properties of materials.

For interpretation of the role of interatomic spacing in the exchange interaction, we can now identify  $\beta$ , a characteristic length, as a parameter that reflects the spatial extension of the  $4f$  wave function. When  $\beta=0$ , we have the  $\delta$ -function approximation, but as  $\beta$  increases from zero the spatial characteristics of the  $4f$  wave functions are introduced. The symbol  $R$  in Eq. (47) has already been identified with  $d$ , the average interatomic spacing. With a given value for  $q$ , the left-hand side of Eq. (47) can be calculated for each of the rare-earth metals by summing the expression on the right-hand side. Here we will include only nearest neighbor interactions, as a first-order approximation. The number of near neighbors is 12, so we can write

$$\frac{T_b}{12C_1(g-1)^2 j(j+1)} = \frac{\cos q_0 R}{\beta R [1 + (R/2\beta)^2]} \quad (48)$$

We note that  $C_1$  is a parameter which is also a property of the rare-earth metals as can be seen from Eq. (46). The resulting interaction curve (calculated) is given in Fig. 2 for the values  $\beta = 0.8$  a. u.,  $q_0 = 8.2\pi$  a. u.<sup>-1</sup>, and  $A = 1.5$ . It is inter-

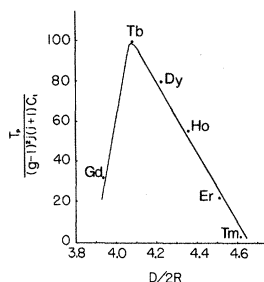


FIG. 2. Exchange-interaction curve for the ferromagnetic rare-earth metals (based on trial functions used herein).

esting to compare it with the experimental curve given in Fig. 1. Qualitative agreement is obtained between theory and experiment, especially as far as the sensitivity to interatomic spacing is concerned. That the relative values of the ordinates in Fig. 1 are not the same as those in Fig. 2 presents no major problem in that  $C_1$ , in Eq. (47), varies from substance to substance.

The second pertinent aspect which we consider is the variation of the interlayer turn angle  $\phi_0$  from one rare-earth element to the other. In passing through the periodic table this angle increases from  $0^\circ$  for Gd to  $50^\circ$  for Ho (at the Néel temperature). In the Heisenberg approximation the exchange energy between localized magnetic moments is written as

$$-\sum_{i,j} \mathcal{J}(R_{ij}) \vec{s}_i \cdot \vec{s}_j,$$

which, for the helical-screw structure, is proportional to the Fourier transform of  $\mathcal{J}(R_{ij})$ , viz.,

$$\mathcal{J}(Q) = \sum_j \mathcal{J}(R_{ij}) e^{i\vec{Q} \cdot \vec{R}_{ij}} \quad (49)$$

The product  $\vec{Q} \cdot \vec{R}_{ij}$  is equal to the turn angle between moments at lattice sites  $i$  and  $j$ .

If  $\mathcal{J}(R_{ij})$  is taken to be the RKKY interaction [ $\beta=0$  in Eq. (35)], then  $\mathcal{J}(Q)$  is a maximum (or the exchange energy is a minimum) for an interlayer turn angle of about  $52^\circ$ . This RKKY interaction accounts for the existence of the helical structure, but not for the variations in turn angle among the elements.

We now examine the exchange interaction of Eq. (35) to determine whether it can account for the variation of  $\phi_0$  among the elements. As in the interpretation of pressure effects, discussed above, the parameter  $\beta$  is associated with the spatial distribution of the  $4f$  electrons; the manner in which this association is formally made is discussed below. For  $\beta=0$  the  $4f$  electrons are highly localized (i. e., a  $\delta$  function) at the nucleus; as  $\beta$  departs from zero, the spatial distribution of the  $4f$  electrons, described by  $F(r)$ , spreads out. Since a small, nonzero value of  $\beta$  "perturbs" the  $\delta$  function,  $(R_{ij})$  can be considered as a perturbed Ruderman-Kittel interaction for small values of  $\beta$ . Among the rare-earth elements which possess helical ordering, the element Ho has the most localized  $4f$  electrons; we therefore associate the  $\delta$ -function approximation with this element (i. e.,  $\beta$  is set equal to zero for Ho). The values of  $\beta$  for the other elements are determined in terms of the "spreading out of the  $4f$  electrons" relative to the element Ho. A natural definition of  $\beta$  for the other elements is then simply

$$\beta = (\langle R_f^2 \rangle)^{1/2} - (\langle R_f^2(\text{Ho}) \rangle)^{1/2},$$

where  $\langle R_f^2 \rangle$  is the average value of  $r^2$  with respect to the radial part of the  $4f$  wave function as deter-

mined for the free ions by Freeman and Watson<sup>11</sup>;  $\langle R_f^2(\text{Ho}) \rangle$  is that value for the particular element holmium. In Fig. 3, the curve labeled  $\phi_0$  (expt) shows the variation of the turn angle among the elements versus the quantity  $\langle R_f^2 \rangle^{1/2} - \langle R_f^2(\text{Ho}) \rangle^{1/2}$ . For the element Gd and for Gd-Dy alloys with greater than 50% Dy, the turn angle is zero<sup>4</sup>; the value of  $\beta$  for the 50-50 Gd-Dy alloy is taken as the average between  $\beta$  of Gd and Dy.

In order to compare theory with experiment, we identify  $\phi_0$  with the angle which maximizes the Fourier transform of  $\mathcal{J}(R_{ij})$ , Eq. (49), where  $\mathcal{J}(R_{ij})$  is the complete exchange interaction given by Eq. (35). Calculations were made of  $\mathcal{J}(Q)$  by evaluating the lattice summations of Eq. (49) in real space with the aid of an electronic computer; over 800 lattice sites were included in the summations. While nearest-neighbor interactions alone were considered in the discussion of pressure effects, this approach is inadequate for studying the turn-angle behavior since nearest-neighbor interactions alone do not yield a helical structure.

Figure 4 shows the behavior of  $\mathcal{J}(Q)$  as a function of turn angle  $\phi$  for three values of  $\beta$  ( $q_0 = 1.1$ ); Table I shows the variation of  $\mathcal{J}(0)$ ,  $\phi_0$ , and the maximum value of  $\mathcal{J}(Q)$  (which occurs at  $\phi = \phi_0$ ) as a function of  $\beta$  for  $q_0 = 1.1$ . It is seen that for this value of  $q_0$ , as  $\beta$  increases, the equilibrium value

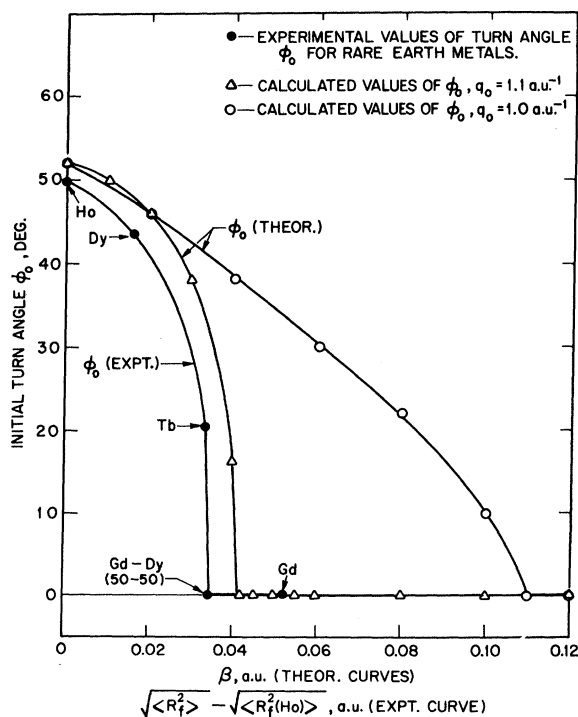


FIG. 3. Comparison between experimental and theoretical values of interlayer turn angle.

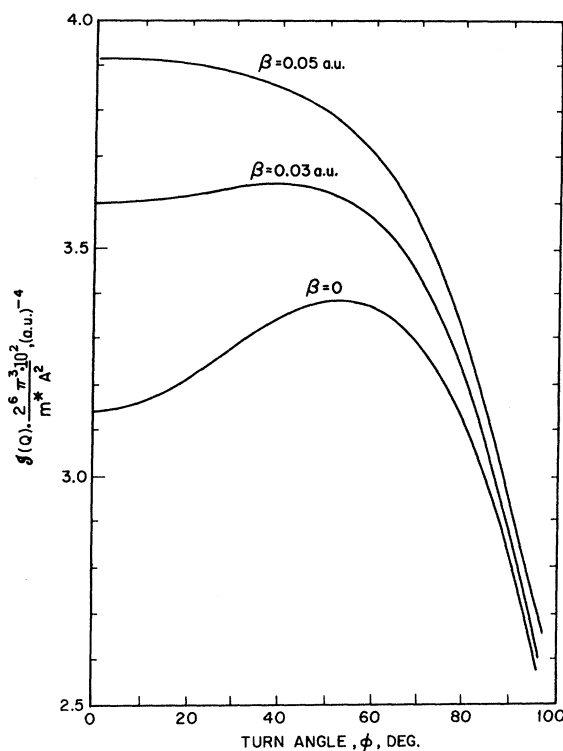


FIG. 4. Variation of  $\mathcal{J}(Q)$  as a function of interlayer turn angle  $\phi$  for  $q=1.1$  and  $\beta=0, 0.03$ , and  $0.05$ . The minimum in exchange energy and corresponding maximum in  $\mathcal{J}(Q)$  occurs at  $\phi = \phi_0$ ; for  $\beta=0, 0.03$ , and  $0.05$ , respectively,  $\phi_0 = 52^\circ, 38^\circ$ , and  $0^\circ$ .

of turn angle decreases from  $52^\circ$  at  $\beta=0$  to  $0^\circ$  at  $\beta=0.042$ . The theoretical dependence of  $\phi_0$  upon  $\beta$  is shown in Fig. 3 for two values of  $q_0$ , viz.,  $q_0 = 1.0$  and  $1.1$ . The quantity  $q_0$  is treated as an

TABLE I. Properties of  $\mathcal{J}(Q)$  calculated as a function of  $\beta$  ( $q_0 = 1.1$  and  $\Lambda = 2^6 \pi^3 \cdot 10^2 / m^* A^2$ ).

$\beta$ (a. u.)	$\mathcal{J}(0) \cdot \Lambda$ (a. u. $^{-4}$ )	Max. value of	
		$\mathcal{J}(Q) \cdot \Lambda$ (a. u. $^{-4}$ )	$\phi_0$ (deg)
0	-3.1419	-3.3851	52
0.01	-3.2917	-3.4590	50
0.02	-3.4443	-3.5425	46
0.03	-3.5997	-3.6388	38
0.04	-3.7579	-3.7583	16
0.042	-3.7898	-3.7898	0
0.045	-3.8380	-3.8380	0
0.05	-3.9189	-3.9189	0
0.055	-4.0005	-4.0005	0
0.06	-4.0828	-4.0828	0
0.08	-4.4195	-4.4195	0
0.10	-4.7682	-4.7682	0
0.12	-5.1294	-5.1294	0
0.20	-6.7093	-6.7093	0
0.30	-9.0355	-9.0355	0



adjustable parameter. There is excellent quantitative agreement between theory and experiment for the case of  $q_0 = 1.1$ . It is noted that  $\beta$  was arbitrarily set equal to zero for the element Ho; this reference could easily be shifted in which case the theoretical and experimental curves would essentially coincide.

Our general conclusion is that the RKKY theory seems to provide the basic mechanism for the origin of ferromagnetism in the rare metals. Using the exchange energy  $J(\vec{k}', \vec{k})$  in Eq. (3) as a parameter is satisfactory when applied to the nuclear-spin interaction, but is like the perfect-gas approximation when applied to the rare earths in that the interesting phenomena are not described. Our contribution has been like that of the van der Waals gas approximation, in that the interesting phenomena are given; also like the van der Waals approximation, it is phenomenological, yet has its

foundation in theory.

Perhaps it might be desirable to interchange the Fourier-transform pairs given in Eqs. (13), (20), and (36) by writing Eq. (38) as an approximation to the  $4f$  distribution first, assign the proper  $\beta$ 's, etc., and then to calculate the  $J(\vec{k}, \vec{k})$  from it. We do not assert that the function used in Eq. (20) is the only way (or even the best way) that the exchange-coupling parameter can be modified. We do show that a very simple function, which can yield analytical results in essentially closed forms, can at the same time provide a semiquantitative explanation of experimental results.

We note that Evenson and Liu<sup>22</sup> have used a somewhat similar  $J(q)$  in discussing a different problem. They were interested in the generalized susceptibility of the ferromagnetic rare-earth metals. In this connection, they used  $J^2(q) = J^2(0) \times \exp[-(q/q_0)^2]$ .

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