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Exchange Interaction in Alloys with Cerium Impurities*

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Starting with the Anderson model for the $4f^1$ configuration of cerium, the transformation of Schrieffer and Wolff is performed, taking into account combined spin and orbit exchange scattering. The resultant interaction Hamiltonian differs qualitatively from the conventional s-f exchange interaction. The Kondo effect, the spin-disorder resistivity, the Ruderman-Kittel interaction, and the depression of the superconducting transition temperature with impurity concentration are worked out for alloys containing cerium impurities on the basis of this new interaction.

1. INTRODUCTION

THE occurrence of a resistivity minimum at low temperatures—or the Kondo effect—has been extensively studied for transitional alloys; magnetic alloys with transition impurities show a Kondo effect, while nonmagnetic alloys do not exhibit a Kondo effect. On the other hand, in the series of dilute alloys with rare-earth impurities in lanthanum or yttrium, the alloys with cerium impurities are the only ones that show a resistivity minimum at low temperatures; all the other rare-earth alloys, though magnetic, do not show a resistivity minimum.[1–7] The anomalous behavior of cerium metal and alloys has been recently studied in detail.[8] In these cases the $4f$ level is very close to the Fermi level, and resonant scattering theory explains their properties. In the other rare earths, the $4f$ levels are generally far from the Fermi level, and the ionic model is valid.

To explain the Kondo effect in magnetic dilute alloys with transition impurities, two models are generally considered, the s-d exchange model and the Anderson model, the latter describing the mixing between conduction electrons and localized electrons. Schrieffer and Wolff[9] have shown that, in the limit of small mixing, the Anderson Hamiltonian leads to an exchange-type Hamiltonian.

To explain the experiments of the Kondo effect in rare-earth alloys, the s-f exchange Hamiltonian is generally used.[1,2] Since the orbital angular momentum is unquenched and the spin-orbit coupling is large, the spin-spin (s-f) exchange Hamiltonian is conventionally written as

$$H=-2\Gamma(g-1)\mathbf{s}\cdot\mathbf{j}\,, \tag{1}$$

where Γ is the interaction constant, g is the Lande g factor, $\mathbf{s}$ is the conduction-electron spin density at the impurity site, and $\mathbf{j}$ is the total angular momentum of the rare-earth impurity. The form of (1) leads to a rather puzzling result, namely, in the case of cerium alloys, $g-1$ is negative, so that there would be a Kondo effect only if Γ were positive, in contrast to transition alloys. Since it is presumed that the strong s-f hybridization in cerium is responsible for the Kondo effect in dilute cerium alloys, while one knows that hybridization exchange leads to *negative* Γ, at least for s-state ions, the origin of the Kondo effect in cerium alloys is unclear.

To clarify the situation, we consider an Anderson-type model for the $4f^1$ configuration of cerium and derive the effective exchange interaction between the conduction electrons and the impurity moment, taking into account combined spin and orbit exchange scattering. Our results differ sharply from the conventional form (1).

The spin-disorder resistivity, the Kondo effect, the Ruderman-Kittel interaction, and the depression of the superconducting transition temperature with impurity concentration are worked out for alloys containing cerium impurities on the basis of this new interaction.

2. EXCHANGE INTERACTION HAMILTONIAN

For a cerium atom, the large spin-orbit coupling leads to a ground state of total angular momentum $j=\frac{5}{2}$ in which the orbital angular momentum ($l=3$) and spin of the f electron are antiparallel; the $j=\frac{7}{2}$ multiplet is widely separated from the ground state and is not of interest here. To treat the mixing of the conduction and impurity wave functions, we work with conduction states that are partial-wave states about the impurity. Since we are only interested in the $l=3$ states of the impurity, and since the conduction-impurity mixing potential is predominantly spherically symmetric, only $l=3$ conduction-electron partial-wave states will enter the problem. Furthermore, it is con-

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[1] T. Sugawara, J. Phys. Soc. Japan **20**, 2252 (1965).

[2] T. Sugawara and H. Eguchi, J. Phys. Soc. Japan **21**, 725 (1966).

[3] T. Sugawara, I. Yamase, and R. Soga, J. Phys. Soc. Japan **20**, 618 (1965).

[4] T. Sugawara and S. Yoshida, J. Phys. Soc. Japan **24**, 1399 (1968).

[5] H. Nagasawa, S. Yoshida, and T. Sugawara, Phys. Letters **26A**, 561 (1968).

[6] T. F. Smith, Phys. Rev. Letters **17**, 386 (1966).

[7] B. Coqblin and C. F. Ratto, Phys. Rev. Letters **21**, 1065 (1968).

[8] B. Coqblin, thesis, Orsay, France, 1967 (unpublished); B. Coqblin and A. Blandin, Advan. Phys. **17**, 281 (1968); B. Coqblin, in Proceedings of the Seventh Rare-Earth Conference, Coronado, Calif., 1968 (unpublished).

[9] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).

venient to make up spin-orbit eigenstates from these partial-wave states so that we work only with states of definite total angular momentum. Let $c_{kM}^\dagger$ create a conduction electron in a state of wave number k, total angular momentum $\frac{5}{2}$, and z component $M(=\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2})$, while $c_{M'}^\dagger$ creates an electron on the impurity with $j=\frac{5}{2}$ and z component M'. Then the Anderson Hamiltonian[10] is

$$H=H_0+H_1, \tag{2a}$$

where

$$H_0=\sum_{k,M}\epsilon_k n_{kM}+E_0\sum_M n_M+\tfrac{1}{2}U\sum_{M,M'}n_M n_{M'}, \tag{2b}$$

$$H_1=\sum_{k,M}(V_k c_{kM}^\dagger c_M+V_k^* c_M^\dagger c_{kM}). \tag{2c}$$

ϵ_k is the energy of a conduction electron of wave number k, and E_0 is the energy of the localized state, both being measured relative to the Fermi energy E_F. We neglect here the multiplet splittings when there are two or more electrons on the impurity, i.e., we neglect atomic exchange integrals compared to the atomic Coulomb integral U.

We follow the method used previously[11] with the same notation was used there. The canonical transformation replaces H_1 by an interaction H_2 which is given by

$$H_2=\tfrac{1}{2}\sum_{abc}\langle b|H_1|c\rangle\langle c|H_1|a\rangle\left(\frac{1}{\epsilon_a-\epsilon_c}+\frac{1}{\epsilon_b-\epsilon_c}\right), \tag{3}$$

where a and b label the initial and final states, respectively. For the $4f^1$ configuration of cerium, these states are of the form

$$|a\rangle=c_{kM}^\dagger c_{M'}^\dagger|0\rangle, \quad |b\rangle=c_{k'M'}^\dagger c_M^\dagger|0\rangle, \tag{4}$$

and the two possible intermediate states for the above states (4) are

$$|c_1\rangle=c_{kM}^\dagger c_{k'M'}^\dagger|0\rangle, \quad |c_2\rangle=c_M^\dagger c_{M'}^\dagger|0\rangle. \tag{5}$$

In this way, we obtain

$$H_2=-\sum_{kk'MM'}J_{kk'}c_{k'M'}^\dagger c_M^\dagger c_{M'}c_{kM}, \tag{6}$$

where

$$J_{k_F,k_F}=|V_{k_F}|^2U/E_0(E_0+U). \tag{7}$$

While $J_{kk'}$ is independent of M and M', it depends on k and k' and is roughly constant so long as $E_0<(\epsilon_k, \epsilon_{k'})<E_0+U$.[3] In the following we take $J_{kk'}$ to be a constant with a cutoff so that $J=0$ if $|\epsilon_k|$ or $|\epsilon_{k'}|>D$, where D is of order $|E_0|$.

The Hamiltonian (6) describes spin and orbit exchange scattering, and, in contrast to the $\mathbf{s}\cdot\mathbf{j}$ exchange model, the change $\Delta M=M'-M$ in the magnetic quantum numbers is not limited to ±1 or 0, as it is for the $\mathbf{s}\cdot\mathbf{j}$ interaction. The form of (6) shows that the magnetic quantum numbers of the conduction and localized electrons are in fact exchanged in the scattering process.

We note that, for a scattering process in which $M=M'$, the average value of (6) over all possible values of $n_M=c_M^\dagger c_M$ is not zero, in contrast to the $\mathbf{s}\cdot\mathbf{S}$ or $\mathbf{s}\cdot\mathbf{j}$ interactions. As a consequence, the interaction (6) actually contains both direct and exchange scattering. For many purposes, it is convenient to remove the direct scattering by adding to (6) the direct potential

$$H_3=\frac{J}{2j+1}\sum_{kMk'M'}c_{k'M'}^\dagger c_{kM'}n_M \tag{8}$$

in order that H_2 and H_3 contain only exchange scattering. Thus, we must subtract from the normal one-electron (direct) potential the term H_3. Thus, the total Hamiltonian is

$$H=\sum_{kM}\epsilon_k n_{kM}-J\sum_{kk'MM'}c_{k'M'}^\dagger c_{kM}\times\left(c_M^\dagger c_{M'}-\frac{\delta_{M,M'}}{2j+1}\sum_{M''}n_{M''}\right), \tag{9}$$

where the k sums are restricted to $|\epsilon_k|<D$. In (9) we have not considered the normal one-electron (direct) potential because it is of no interest for the physical properties studied in the following work. The Hamiltonian (9) reduces to the conventional exchange Hamiltonian for $s=\frac{1}{2}$, the case usually studied.

Since E_0 is small and negative in cerium alloys, such as La-Ce and Y-Ce alloys (E_0 is believed to be of order of a few hundredths to a tenth of an eV), the value of J given by (7) is large and negative, of order several tenths of an eV. Since the normal Heisenberg exchange arising from Coulomb interactions between the conduction and localized electrons is likely a good deal smaller in magnitude than J, we neglect it in the present discussion. We will return to this point later.

The form (9) of the Hamiltonian, using the partial wave operators $c_{kM}^\dagger$ for conduction electrons, is very appropriate to the study of some properties of the cerium alloys, such as the Kondo effect. But, for some other properties, such as the Ruderman-Kittel interaction, it is more convenient to work with plane wave operators $c_{\mathbf{k}\sigma}^\dagger$ for conduction electrons. Let $c_{\mathbf{k}\sigma}^\dagger$ create a conduction electron in a state of wave vector $\mathbf{k}$ and spin σ. Let us note that, in the operator $c_{kM}^\dagger$, the k index is the wave number $k=|\mathbf{k}|$, while in the operator $c_{\mathbf{k}\sigma}^\dagger$, the k index is the wave vector $\mathbf{k}$.

The transformation from the $c_{kM}^\dagger$ operators to the $c_{\mathbf{k}\sigma}^\dagger$ operators can be written as

$$c_{kM}^\dagger=\sum_{\mathbf{k},\sigma}c_{\mathbf{k}\sigma}^\dagger\langle kM|\mathbf{k}\sigma\rangle. \tag{10}$$

The sum in (10) is over the different angles of $\mathbf{k}$ at $|k|$ fixed and over the two spin directions σ; $|\mathbf{k}\sigma\rangle$

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[10] P. W. Anderson, Phys. Rev. **126**, 41 (1961).

[11] J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).

denotes a plane wave of wave vector **k** and spin σ; and $|kM\rangle$ denotes a partial wave of wave number $|k|$, total angular momentum $\frac{5}{2}$, and z component M. Thus, the total Hamiltonian (11) is

$$H=\sum_{\mathbf{k},\sigma}\epsilon_k n_{\mathbf{k}\sigma}-\sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'}\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}c_{\mathbf{k}'\sigma'}{}^{\dagger}c_{\mathbf{k}\sigma}\times\left(c_M{}^{\dagger}c_{M'}-\frac{\delta_{M,M'}}{2j+1}\sum_{M''}n_{M''}\right), \tag{11}$$

where

$$\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}=J\langle\mathbf{k}\sigma|kM\rangle\langle k'M'|\mathbf{k}'\sigma'\rangle. \tag{12}$$

Let us compute the value of $\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}$. For an $l=3$ and $j=\frac{5}{2}$ state, the partial wave $|kM\rangle$ is given as a function of the partial waves $|k,l,m,\sigma\rangle$, where $l=3$, m is the z component of the angular momentum, and σ is the spin

$$|kM\rangle=\alpha_M|k,3,M+\tfrac{1}{2},-\tfrac{1}{2}\rangle+\beta_M|k,3,M-\tfrac{1}{2},\tfrac{1}{2}\rangle, \tag{13}$$

where the two Clebsh-Gordan coefficients α_M and β_M are

$$\alpha_M=[(7+2M)/14]^{1/2},\quad \beta_M=[(7-2M)/14]^{1/2}. \tag{14}$$

The $|k,l,m,\sigma\rangle$ wave function is proportional to $j_l(kr)Y_l{}^m(\theta,\varphi)|\sigma\rangle$, where $j_l(kr)$ is the spherical Bessel function and $Y_l{}^m(\theta,\varphi)$ is the spherical harmonic. Here we choose

$$\langle r,\theta,\varphi|k,l,m,\sigma\rangle=\sqrt{(4\pi)}\,j_l(kr)Y_l{}^m(\theta,\varphi)|\sigma\rangle \tag{15}$$

in order to make contact with the $s=\frac{1}{2}$ case for the Hamiltonian (11). Thus, the plane wave $|\mathbf{k}\sigma\rangle$ is equal to

$$|\mathbf{k}\sigma\rangle=\sqrt{(4\pi)}\sum_{l=0}^{\infty}\sum_{=-l}^{l}i^lY_l{}^{m*}(\Omega_k)|k,l,m,\sigma\rangle. \tag{16}$$

Thus, the calculation of $\mathcal{J}$ gives

$$\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}=4\pi J[\alpha_MY_3{}^{M+\frac{1}{2}}(\Omega_k)\delta_{\sigma,-\frac{1}{2}}+\beta_MY_3{}^{M-\frac{1}{2}}(\Omega_k)\delta_{\sigma,\frac{1}{2}}]\times\{\alpha_{M'}[Y_3{}^{M'+\frac{1}{2}}(\Omega_{k'})]^*\delta_{\sigma',-\frac{1}{2}}+\beta_{M'}[Y_3{}^{M'-\frac{1}{2}}(\Omega_{k'})]^*\delta_{\sigma',\frac{1}{2}}\}. \tag{17}$$

If there are n impurities located at positions R_n, the total Hamiltonian is

$$H=\sum_{\mathbf{k}\sigma}\epsilon_kn_{\mathbf{k}\sigma}-\sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'MM'n}\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n}c_{\mathbf{k}'\sigma'}{}^{\dagger}c_{\mathbf{k}\sigma}\times\left(c_{M'}{}^{\dagger(n)}c_M{}^{(n)}-\frac{\delta_{MM'}}{2j+1}\sum_{M''}n_{M''}{}^{(n)}\right), \tag{18}$$

where $c_M{}^{\dagger(n)}$ corresponds to the nth atom. Thus we have derived an exchange-type Hamiltonian taking into account combined spin and orbit exchange scattering, and the forms (9), (11), and (18) are very useful for the following.

3. RESISTIVITY AND THE KONDO EFFECT

To compute the resistivity and discuss the Kondo properties of cerium alloys, we use the form (9) of the Hamiltonian and outline the Nagaoka equations and the Green's-function truncation scheme employed previously by Nagaoka[12] for the conventional exchange interaction.

Introducing the Zubarev Green's functions

$$\begin{aligned}G_{kk'M}&=\langle c_{k'M}|c_{kM}{}^{\dagger}\rangle,\\ \Gamma_{kk'M}&=\sum_{M'}\langle c_{k'M'}c_{M'}{}^{\dagger}c_M|c_{kM}{}^{\dagger}\rangle-\frac{1}{2j+1}G_{kk'M},\end{aligned} \tag{19}$$

and the averages

$$\begin{aligned}n_{k'}&=\int_{-\infty}^{\infty}[-2\,\mathrm{Im}\sum_kG_{kk'M}(\omega)]f(\omega)d\omega,\\ m_{k'}&=\int_{-\infty}^{\infty}[-2\,\mathrm{Im}\sum_k\Gamma_{kk'M}(\omega)]f(\omega)d\omega,\end{aligned} \tag{20}$$

where $f(\omega)$ is the Fermi function, we obtain two Nagaoka equations[12]

$$\begin{aligned}&(\omega-\epsilon_{k'})G_{kk'M}+J\sum_l\Gamma_{klM}=\delta_{k,k'}/2\pi,\\ &(\omega-\epsilon_{k'})\Gamma_{kk'M}-J\left[(2j+1)m_{k'}-\frac{4j(j+1)}{(2j+1)^2}\right]\sum_lG_{klM}\\ &\qquad+J\left[(2j+1)n_{k'}-\frac{2}{(2j+1)}\right]\sum_l\Gamma_{klM}=0.\end{aligned} \tag{21}$$

The solution of Eq. (21) has the same form as for the $s=\frac{1}{2}$ spin, and we can deduce the following results:

(1) There is a Kondo effect for cerium alloys, because J is negative. The Kondo temperature is given by

$$k_BT_k\simeq D\exp[-1/(2j+1)|J|n(E_F)], \tag{22}$$

where $n(E_F)$ is the density of states of the conduction band at Fermi level for one spin direction.

We note that in (22) the coefficient in the exponential is $2j+1$ and not 2, as for the $\mathbf{s}\cdot\mathbf{S}$ or $\mathbf{s}\cdot\mathbf{j}$ interactions. In fact, there are $2j+1$ channels for changing the quantum number M on the impurity (instead of 2, as for the $\mathbf{s}\cdot\mathbf{S}$ and $\mathbf{s}\cdot\mathbf{j}$ interactions), and these channels add independently to each other. The same result occurs obviously in the Kondo resistivity. In (22) the cutoff D is not the width of the conduction band, but rather the distance E_0 from the $4f$ localized level to the Fermi level, as in superconductivity theory. With E_0 of the order of 0.1 eV and $2j+1=6$, T_k for cerium alloys is of the order of several degrees Kelvin to some 10°, roughly of the same order of magnitude as the experimental values for Y-Ce and La-Ce alloys.[4,5,13]

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[12] Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).

[13] S. A. Edelstein, Phys. Letters **27A**, 614 (1968); Phys. Rev. Letters **20**, 1348 (1968).

(2) Above T_k, there is spin and orbital magnetism. Below T_k, the preceding analysis suggests that there is, in cerium alloys, a compensation of the total angular momentum, i.e., a compensation of both spin and orbital momentum. This has not been investigated at present in detail. However, recent magnetic susceptibility experiments on La-Ce alloys at low temperatures indicate that the effective magnetic moment is $0.5\mu_B$ and is a decreasing function of temperature. Hence the orbital moment has been greatly reduced. So in spite of possible crystalline field arguments, it seems to be the first evidence of combined spin and orbital compensation.[14]

(3) The spin-disorder resistivity is

$$R_s = \frac{2\pi m^* n(E_F)}{ze^2 h} cJ^2 \frac{4j(j+1)}{(2j+1)^2}. \tag{23}$$

m^* is the effective mass and z the number of conduction electrons per unit volume. We will return to this point later.

(4) The exchange scattering resistivity for $T > T_k$ is

$$R = R_s[1 + |J|(2j+1)n(E_F)\ln(0.77D/k_BT)]. \tag{24}$$

There should be a resistivity minimum above T_k and a plateau below T_k. These results are in agreement with recent experiments on Y-Ce alloys.[4]

4. RUDERMAN-KITTEL INTERACTION

We have seen, in the preceding section, that the results derived on the basis of the new exchange-type interaction are different from the results obtained with the $\mathbf{s}\cdot\mathbf{S}$ or $\mathbf{s}\cdot\mathbf{j}$ interactions. It is interesting to look at other properties of magnetic dilute alloys, in order to see if there are other differences. The first interesting property is the Ruderman-Kittel[15] interaction between two magnetic cerium impurities, i.e., the indirect interaction of two cerium impurities via the exchange interaction of their $4f$ shells with the conduction electrons.

Let us consider two impurities 1 and 2 at a distance R. The total second-order interaction between the two magnetic impurities is given by

$$H_{12}(R) = \sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} \frac{\langle \mathbf{k}\sigma | H_i | \mathbf{k}'\sigma' \rangle \langle \mathbf{k}'\sigma' | H_i | \mathbf{k}\sigma \rangle}{\epsilon_k - \epsilon_{k'}}. \tag{25}$$

H_i is the interaction Hamiltonian given by the second term of the expression (18). The sum in (25) is for all the filled $\mathbf{k}$ values and all the empty $\mathbf{k}'$ values.

The expression (25) corresponds to all the changes from M to M' on the impurity 1 and the corresponding changes from M' to M on the impurity 2. Thus $H_{12}(R)$ can be written as

$$H_{12}(R) = \sum_{MM'} \Bigg[E_{12}{}^{MM'}(R) \times\left(c_{M'}{}^{\dagger(1)} c_M{}^{(1)} - \frac{\delta_{M,M'}}{2j+1} \sum_{M''} n_{M''}{}^{(1)} \right) \times\left(c_M{}^{\dagger(2)} c_{M'}{}^{(2)} - \frac{\delta_{MM'}}{2j+1} \sum_{M''} n_{M''}{}^{(2)} \right) \Bigg]. \tag{26}$$

$E_{12}{}^{MM'}(R)$ is the interaction energy for an individual change from M to M' on 1 and the corresponding change from M' to M on 2. Using the fact that $(\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'})^* = \mathcal{J}_{k'\sigma' k\sigma}{}^{M'M}$, we obtain the value of $E_{12}{}^{MM'}(R)$ from

$$E_{12}{}^{MM'}(R) = 2 \sum_{k\sigma k'\sigma'} \frac{f_k(1-f_{k'})}{\epsilon_k - \epsilon_{k'}} \times |\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}|^2 \cos(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}, \tag{27}$$

where f_k is the Fermi-Dirac function for the energy ϵ_k. We see that the terms in the parentheses are identical by interchange of k and k', so that the terms in $f_k f_{k'}$ vanish, since the denominators are of the opposite sign. Hence we have

$$E_{12}{}^{MM'}(R) = 2 \sum_{k\sigma k'\sigma'} \frac{f_k}{\epsilon_k - \epsilon_{k'}} \times |\mathcal{J}_{k\sigma k'\sigma'}{}^{MM'}|^2 \cos(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}. \tag{28}$$

We use the form (17) of $\mathcal{J}$ and we expand the plane waves in partial waves. For this we take the z axis along the line connecting the impurities 1 and 2. Hence we have

$$e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = \sum_{l,l'=0}^{\infty} (2l+1)(2l'+1) j_l(kR) j_{l'}(k'R) \times P_l(\cos\theta_k) P_l(\cos\theta_{k'}). \tag{29}$$

We separate the integration in (28) into an integration over the magnitudes $|\mathbf{k}|$ and $|\mathbf{k}'|$ and an integration over the angles of k and k'. At last, we obtain

$$E_{12}{}^{MM'}(R) = \frac{J^2 m^*}{\pi^4} \sum_{ll'} (2l+1)(2l'+1) \times B_l(M) B_{l'}(M') I_{ll'}(R), \tag{30}$$

where

$$B_l(M) = \alpha_M{}^2 \int d\Omega_k\, P_l(\cos\theta_k) |Y_3{}^{M+\frac{1}{2}}(\Omega_k)|^2 + \beta_M{}^2 \int d\Omega_k\, P_l(\cos\theta_k) |Y_3{}^{M-\frac{1}{2}}(\Omega_k)|^2, \tag{31}$$

$$I_{ll'} = \int_0^{k_F} k^2 j_l(kR) dk \int_0^{\infty} \frac{k'^2}{k^2 - k'^2} j_{l'}(k'R) dk'.$$

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[14] A. S. Edelstein (private communication).

[15] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vol. II, Appendix 20.

The value of $B_l(M)$ is easily obtained as a function of the coefficients $C_l(3,m;3,m)$ introduced by Slater[15] for the addition of three angular momenta

$$B_l(M)=\alpha_M{}^2C^l(3,M+\tfrac{1}{2};3,M+\tfrac{1}{2})+\beta_M{}^2C^l(3,M-\tfrac{1}{2};3,M-\tfrac{1}{2}).\qquad(32)$$

The only nonzero $C^l(3,m;3,m)$ coefficients correspond to $l=0$, 2, 4, 6. In particular, $C^0(3,m;3,m)$ is always equal to 1.

On the other hand, the integrals $I_{ll'}(R)$ are not in general easy to compute. The first one I_{00} for $l=l'=0$ can be computed exactly and gives the classical Ruderman-Kittel interaction[16]

$$I_{00}(R)=\pi k_F{}^4F(2k_FR),$$

with

$$F(x)=(x\cos x-\sin x)/x^4.\qquad(33)$$

Thus, the first term gives the classical Ruderman-Kittel interaction for a $s=\frac{1}{2}$ spin and is independent of M and M'. However, the terms other than $l=l'=0$ in the expression (30), which depend on the M and M' values, are not small compared to the first term and have to be taken into account. The dependence of these terms on M and M' gives an anisotropic Ruderman-Kittel interaction.

Fortunately, it is easy to compute the asymptotic form of $I_{ll'}(R)$ when $k_FR\rightarrow\infty$, which is generally the only term considered in the Runderman-Kittel interaction for experimental purpose. The asymptotic form of the Bessel function is

$$j_l(kR)\cong\sin(kR-\tfrac{1}{2}l\pi)/kR,\quad R\rightarrow\infty\qquad(34)$$

so that the asymptotic form of $I_{ll'}(R)$ for $k_FR\rightarrow\infty$ is

$$I_{ll'}(R)\simeq\pi k_F{}^4\cos[2k_FR-\tfrac{1}{2}\pi(l+l')]/(2k_FR)^3.\qquad(35)$$

Since $l+l'$ is always even, the phase of the cosine in the expression (35) gives only a factor $(-1)\frac{1}{2}(l+l')$. If we call

$$F(M)=\sum_{l=0,2,4,6}(-1)^{l/2}(2l+1)\times[\alpha_M{}^2C^l(3,M+\tfrac{1}{2};3,M+\tfrac{1}{2})+\beta_M{}^2C^l(3,M-\tfrac{1}{2};3,M-\tfrac{1}{2})],\qquad(36)$$

and

$$G(M,M')=F(M)F(M'),$$

the asymptotic form of the interaction $E_{12}{}^{MM'}$ is

$$E_{12}{}^{MM'}(R)\simeq(m^*k_F{}^4J^2/\pi^3)G(M,M')\times\cos(2k_FR)/(2k_FR)^3,\quad R\rightarrow\infty\qquad(37)$$

and the total interaction is given by (26).

The coefficients $G(M,M')$ are simple to compute, and there are relations between them:

$$G(M,M')=G(M',M)=G(|M|,|M'|).\qquad(38)$$

Thus, there remain only the six coefficients

$$G(\tfrac{5}{2},\tfrac{5}{2})=400/49,\quad G(\tfrac{3}{2},\tfrac{3}{2})=16/49,\quad G(\tfrac{1}{2},\tfrac{1}{2})=25/49,$$
$$G(\tfrac{5}{2},\tfrac{3}{2})=-80/49,\quad G(\tfrac{5}{2},\tfrac{1}{2})=100/49,\quad G(\tfrac{3}{2},\tfrac{1}{2})=-20/49.$$

The average value of $G(M,M')$ is equal to 1.

The form (37) of the Ruderman-Kittel interaction is strongly anisotropic, owing to the different values of the $G(M,M')$ coefficients. To our knowledge this has never been looked for experimentally. The analysis of the experiments involving the Ruderman-Kittel interaction in alloys with cerium impurities and in cerium compounds should be repeated on the basis of this new anisotropic interaction.

5. DEPRESSION OF SUPERCONDUCTING TRANSITION TEMPERATURE

The superconducting transition temperature T_c for solid solutions of cerium in lanthanum has been measured both at normal pressure[2] and as a function of pressure.[6] An explanation has been presented by Sugawara,[2] by use of $\mathbf{s}\cdot\mathbf{j}$ or $\mathbf{s}\cdot\mathbf{S}$ interactions, for the normal pressure experiments. A recent analysis of the pressure-dependent experiments has been made by use of the $\mathbf{s}\cdot\mathbf{S}$ interaction.[7] It is obviously interesting to check this analysis on the basis of the new Hamiltonian. The decrease ΔT_c of the superconducting transition temperature with concentration C of cerium impurities is given by[17]

$$\Delta T_c=-\tfrac{1}{2}\pi^2[n(E_F)/k_B]C\langle\langle|\langle\mathbf{k}\sigma|H_i|\mathbf{k}'\sigma'\rangle|^2\rangle\rangle,\qquad(39)$$

where $\langle\langle\cdots\rangle\rangle$ means the average over the solid angle between $\mathbf{k}$ and $\mathbf{k}'$, over the spins σ and σ', and over the orientations of the impurity magnetic moment.

We use the form (11) for the interaction Hamiltonian H_i. The average over the angles of $\mathbf{k}$ and $\mathbf{k}'$ and the spins σ and σ' is easily carried out, and we have

$$\langle\langle|\langle\mathbf{k}\sigma|H_i|\mathbf{k}'\sigma'\rangle|^2\rangle\rangle=J^2\left\langle\sum_{MM'}\left(c_{M'}{}^\dagger c_M-\frac{\delta_{MM'}}{2j+1}\sum_{M''}n_{M''}\right)\times\left(c_M{}^\dagger c_{M'}-\frac{\delta_{MM'}}{2j+1}\sum_{M''}n_{M''}\right)\right\rangle,\qquad(40)$$

where $\langle\cdots\rangle$ denotes the average only over the orientation of the impurity magnetic moment. Therefore we have

$$\langle\langle|\langle\mathbf{k}\sigma|H_i|\mathbf{k}'\sigma'\rangle|^2\rangle\rangle=4J^2j(j+1)/(2j+1)^2,\qquad(41)$$

and one finds that

$$\frac{dT_c}{dC}=-\frac{\pi^2n(E_F)}{2k_B}J^2\frac{4j(j+1)}{(2j+1)^2}.\qquad(42)$$

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[16] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); K. Yosida, *ibid.* **106**, 893 (1957).

[17] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

Thus, the decrease of T_c with the concentration C of cerium impurities has the same form as that obtained with the $\mathbf{s}\cdot\mathbf{S}$ or $\mathbf{s}\cdot\mathbf{j}$ Hamiltonian, but with a different coefficient. We will return to this point in the next section.

6. COMPARISON WITH EXPERIMENTS

In this section, we point out the differences between this new Hamiltonian and the two normal $\mathbf{s}\cdot\mathbf{S}$ and $\mathbf{s}\cdot\mathbf{j}$ Hamiltonians.[18] We deduce the values of the interaction constant J for cerium alloys and the corresponding value E_0 of the separation between the $4f$ localized level and the Fermi level.

Table I summarizes the results obtained with the three Hamiltonians for cerium alloys for which $J<0$. For cerium impurities, we have $s=\frac{1}{2}$, $j=\frac{5}{2}$, $g-1=-\frac{1}{7}$.

The main physical difference between the two conventional Hamiltonians H_s and H_j and this new Hamiltonian H are the following:

(1) For the spin disorder resistivity R_s and for the decrease of the superconducting temperature T_c with concentration C, the results are qualitatively the same for the three Hamiltonians. There is only a change in the coefficient coming from the magnetic moment of the impurity. For the various Hamiltonians this coefficient is

$$H_s \to s(s+1)=\tfrac{3}{4}\,,$$
$$H_j \to (g-1)^2 j(j+1)=5/28\,,$$
$$H \to 4j(j+1)/(2j+1)^2=35/36\,.$$

For numerical applications, H_s and H give almost the same results, while H_j gives different results.

(2) For the asymptotic form of the Ruderman-Kittel interaction $E_{12}^{MM'}(R)$ between two impurities, the result is not even qualitatively the same. H_s and H_j give an isotropic interaction, while H gives a strongly anisotropic interaction. In fact, these differences can be easily understood, because H_s and H_j are both built with $l=0$ type states while H is built with real $l=3$ states.

(3) The main difference comes in the Kondo effect. With a negative value for J, H_j gives no Kondo effect for cerium alloys, in contrast to the experimental results.[1,2] H_s and H both give the Kondo effect with different coefficients.

The second point we consider is the derivation of J and E_0 from the experiments. The Ruderman-Kittel interaction is at present not useful for this purpose because there are not experiments relating to it in cerium alloys. The Kondo properties are not precise enough to give the absolute value of J, but they can give a definite result for the sign of J. J is negative in Y-Ce and La-Ce alloys because they present a Kondo effect.[1,2] Then we can use the spin disorder resistivity and the depression of the superconducting temperature in order to obtain the value of J.[1,2,6]

The value of the density of states of the conduction band for pure lanthanum and pure yttrium has been deduced from specific heat data.[19] The density of states can be taken as $n(E_F)=2.2$ states/eV at. and the effective mass $m^*=3$ for the two lanthanum and yttrium hosts.[18] But, in fact, the conduction band is composed of both a $6s$ band and a narrow $5d$ band. Band calculations on yttrium[20] have shown that the contribution of the $6s$ electrons at the Fermi level is small compared to the contribution of the $5d$ electrons. We estimate the contribution of the $6s$ electron to be $n(E_F)=0.5$ states/eV at. and $m^*=1$.

TABLE I. Comparisons among the three Hamiltonians for cerium alloys for which $J<0$.

Hamiltonian	$H_s=-2J\mathbf{s}_c\cdot\mathbf{S}$	$H_j=-2J(g-1)\mathbf{s}_c\cdot\mathbf{j}$	$H=-J\sum_{kk'MM'} c_{k'M'}{}^{\dagger}c_M{}^{\dagger}c_{M'}c_{kM}$
Spin-disorder resistivity R_s	$\dfrac{2\pi m^* n(E_F)cJ^2 s(s+1)}{ze^2\hbar}$	$\dfrac{2\pi m^* n(E_F)cJ^2(g-1)^2 j(j+1)}{ze^2\hbar}$	$\dfrac{2\pi m^* n(E_F)cJ^2}{ze^2\hbar}\dfrac{4j(j+1)}{(2j+1)^2}$
Depression of the superconducting temperature dT_c/dC	$-\frac{1}{2}\pi^2\dfrac{n(E_F)}{k_B}J^2 s(s+1)$	$-\frac{1}{2}\pi^2\dfrac{n(E_F)}{k_B}J^2(g-1)^2 j(j+1)$	$-\frac{1}{2}\pi^2\dfrac{n(E_F)J^2}{k_B}\dfrac{4j(j+1)}{(2j+1)^2}$
Asymptotic form of the Ruderman-Kittel interaction $E_{12}^{MM'}(R)$	$\dfrac{J^2 m^* k_F{}^4}{\pi^3}\dfrac{\cos 2k_F R}{(2k_F R)^3}(2\mathbf{S}_1\cdot\mathbf{S}_2)_{MM'}$	$\dfrac{J^2 m^* k_F{}^4}{\pi^3}\dfrac{\cos 2k_F R}{(2k_F R)^3}(g-1)^2(2\mathbf{J}_1\cdot\mathbf{J}_2)_{MM'}$	$\dfrac{J m^* k_F{}^4}{\pi^3}\dfrac{\cos 2k_F R}{(2k_F R)^3}G(M,M')$
Kondo temperature T_k	$T_k=D\exp\left[\dfrac{-1}{2\lvert J\rvert n(E_F)}\right]$	No Kondo effect	$T_k=D\exp\left[\dfrac{-1}{(2j+1)\lvert J\rvert n(E_F)}\right]$
Kondo resistivity R	$R_{0s}\left[1+2\lvert J\rvert n(E_F)\ln\dfrac{0.77D}{k_B T}\right]$	No Kondo effect	$R_{0s}\left[1+(2j+1)Jn(E_F)\ln\dfrac{0.77D}{k_B T}\right]$

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[18] P. G. de Gennes, J. Phys. Radium **23**, 510 (1962).

[19] K. Andres, Phys. Rev. **168**, 708 (1968); T. Satoh and T. Ohtsuka, J. Phys. Soc. Japan **23**, 9 (1967).

[20] T. L. Loucks, Phys. Rev. **144**, 504 (1966).

Table II gives the values of $2J$ computed in the two limit cases, namely, $n(E_F)=2.2$ states/eV at. and $m^*=3$, which gives a lower limit for $|J|$, and $n(E_F)=0.5$ states/eV at. and $m^*=1$, which gives an upper limit for $|J|$. Table II gives also the corresponding values of E_0. Because the Coulomb integral U is much larger than E_0 in cerium alloys, J reduces to the simple form

$$J\simeq|V_{k_F}|^2/E_0\,. \qquad (43)$$

We can compute E_0 either as a function of the Hartree-Fock half-width of the level, as previously done,[7] or directly, by taking a reasonable value for the mixing parameter V_{k_F}. We cannot hope for better than a rough magnitude agreement, and we use a value $V_{k_F}=0.07$ eV in the calculations of Table II. The values of $|E_0|$ are slightly overestimated because we have not considered here the normal Heisenberg exchange interaction.[7]

The results of Table II must be analyzed carefully. In a resistivity experiment, for example, a current is given almost exclusively by $6s$ electrons, so that the values of $2J$ and E_0 which we deduce from this experiment correspond roughly to the $6s$ band parameters $n(E_F)=0.5$ states/eV at. and $m^*=1$. On the other hand, both $6s$ and $5d$ electrons contribute to the superconductivity mechanism, and the values of $2J$ and E_0 will be rather close to the values corresponding to the total conduction-band parameters $n(E_F)=2.2$ states/eV at. and $m^*=3$.

Therefore, this analysis gives the following results:

(1) In Y-Ce alloys, the value of $2J$ is of order -0.4 eV and the $4f$ level lies an order of 0.03 eV below the Fermi level. The effect of pressure will be particularly large in this case, because the $4f$ level is extremely close to the Fermi level. Because of the extreme smallness of E_0 in Y-Ce alloys, the second-order formula (43) is relatively dubious at normal pressure and cannot give better than an order of magnitude for E_0. Moreover, this formula should not be valid for high-pressure experiments, because E_0 tends to zero.

(2) In La-Ce alloys, the value of $2J$ is smaller, of order -0.1 eV, and the $4f$ level lies roughly 0.1 eV below the Fermi level. The effect of pressure on the superconducting transition temperature has been already studied and gives an important increase of $|J|$ (by $\frac{1}{3}$ under a 10 kbar pressure) and a corresponding important decrease of E_0.[6,7]

In the above discussion, we have neglected the Heisenberg exchange, although, as we mentioned, it is no doubt dominated by the strong hybridization exchange in Ce and should not modify our conclusion. In addition, we have studied only the $4f^1$ configuration and have not treated rare earths other than Ce. For the $4f^n$ configurations ($n>1$), the angular momentum algebra is more involved and has been treated in a different model by Watson, Koide, Peter, and Freeman.[21] Since the hybridization exchange is no doubt less important in these other rare earths, they are of less interest from the above point of view.

TABLE II. Values of $2J$ and E_0 for La-Ce and Y-Ce alloys.

	$n(E_F)=0.5$ states/eV at. $m^*=1$	$n(E_F)=2.2$ states/eV at. $m^*=3$
Y-Ce alloys (from spin-disorder resistivity)	$2J=-0.43$ eV $E_0=-0.025$ eV	$2J=-0.12$ eV $E_0=-0.08$ eV
La-Ce alloys (from spin-disorder resistivity)	$2J=-0.14$ eV $E_0=-0.07$ eV	$2J=-0.04$ eV $E_0=-0.25$ eV
La-Ce alloys (from superconducting temperature)	$2J=-0.18$ eV $E_0=-0.055$ eV	$2J=-0.08$ eV $E_0=-0.12$ eV

We note that the $4f^{13}$ configuration (one $4f$ hole) can be treated as above by interchanging holes and electrons. Thus, the preceding results can be applied to magnetic ytterbium alloys, with a total angular momentum $j=\frac{7}{2}$. In this regard, a resistance minimum has been recently reported in some silver-gold alloys containing ytterbium impurities.[22]

The preceding analysis suggests several types of experiments:

(1) Look in detail for a spin and orbit compensated state at temperatures below T_k in Ce alloys, such as La-Ce and Y-Ce, by methods used for transition impurities.

(2) Look for changes of T_k and other Kondo properties with pressure, since E_0 is likely to be a strong function of pressure.[7,8] Perhaps one can see the disappearance of magnetism and the Kondo effect at very high pressure in La-Ce and Y-Ce alloys.

(3) By comparing various transport and magnetic properties, establish the validity of the new exchange interaction (6) relative to the conventional s-f interactions.

7. CONCLUSION

Thus, we have derived an exchange Hamiltonian and have accounted for various properties for the $4f^1$ configuration of cerium. This analysis gives a consistent description of the resistance minimum and resolves the difficulties encountered by the conventional s-f exchange model. New results for the spin-disorder resistivity and the depression of the superconducting temperature versus impurity concentration have been derived, and a strongly anisotropic Ruderman-Kittel interaction has been obtained.

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[21] R. E. Watson, S. Koide, M. Peter, and A. J. Freeman, Phys. Rev. **139**, A167 (1965).

[22] J. Boes, A. J. Van Dam, and J. Bijovet, Phys. Letters **28A**, 101 (1968).