Hybridization and Kondo effect in systems with degenerate *d* and *f* shells

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The dependence of the hybridization matrix elements between conduction electrons and localized $d(f)$ states on many-electron quantum numbers of atomic configurations is investigated. The corresponding anisotropic $s-d(f)$ exchange interaction is derived. The electron Green's functions for one-impurity and periodic Anderson model are calculated, and expressions for the Kondo temperature, with allowance for the many-electron term structure, are obtained. Experimental data on the Kondo effect for transition metal impurities are discussed. © *1995 American Institute of Physics.*

1. INTRODUCTION

Since Kondo's[1] explanation of the logarithmic anomaly in the electrical resistivity of diluted transition metal alloys on the basis of the $s-d$ exchange model, the problem of the Kondo effect (resonance scattering of conduction electrons by localized magnetic moments) has attracted the interest of many researchers. The Kondo effect plays an important role not only in diluted d systems, but also in a number of $4f$ and $5f$ compounds. Some of them (heavy-fermion systems, "Kondo lattices") exhibit anomalous electronic and magnetic properties. The unusual "Kondo" state, which is characterized by quenched magnetic moments and strongly enhanced electronic specific heat and paramagnetic susceptibility, occurs below a characteristic Kondo temperature T_K, which corresponds to the divergence of the perturbation series.

The Kondo problem is very difficult and leads to elegant mathematics. The one-impurity $s-d$ model was solved with use of the numerical and analytical renormalization group method,[2] and by Andrei and Wiegmann (see Ref. 3) with use of the exact analytical Bethe ansatz approach. These results were obtained on the basis of simple theoretical models which ignore atomic orbital momenta and are apparently insufficient to describe quantitatively the real electronic structure of most Kondo impurities.

Experimental data on the Kondo temperature for the whole series of d impurities in copper and gold, which were obtained from various physical properties, are presented in Ref. 4. The dependence on the d-electron number demonstrates a sharp minimum in the middle of the series. Such a dependence was qualitatively explained by using the results of Schrieffer.[5] However, as discussed in Ref. 6, the theoretical model used in Ref. 5 may be justified only in the case of a low-symmetry crystal field or very strong Jahn-Teller effect, which fully eliminates scattering by orbital degrees of freedom. The latter play an important role for transition metal ions (see, e.g., Ref. 7). An estimate of the Kondo temperature for real atomic configurations was attempted in Ref. 6 with use of the irreducible tensor operator approach in the $s-d$ model with orbital degrees of freedom. An account of the LS term and the crystalline electric field (CEF) splitting, which arises from summation of the Clebsh–Gordan coefficients, led to the reduction of T_K in the middle of the $3d$ series, which agreed with the experimental data. At the same time, the agreement was not quite satisfactory.

In the present paper we investigate the Kondo problem, beginning with the Anderson model with real atomic configurations, both for the single impurity and lattice cases. This model enables one to take into account the energy splitting of $d(f)$-levels in the energy denominators. It reduces to the $s-d$ exchange model used in Ref. 6 only when this splitting is disregarded.[8] In Sec. 2, we formulate the model and derive the dependence of the effective hybridization matrix elements on many-electron quantum numbers. In Sec. 3, we analyze the corresponding anisotropic $s-d(f)$ exchange interaction. In Sec. 4, we calculate the electron Green's function in the degenerate Anderson model, and estimate the hybridization gap and the Kondo temperature. The experimental results are discussed in Sec. 5. In Appendix I we calculate the Kondo temperature from perturbation theory in a simple $s-d$ exchange model without intraconfiguration splitting.

2. DEGENERATE ANDERSON MODEL AND EFFECTIVE HYBRIDIZATION PARAMETERS

Disregarding spin-orbit coupling, which is a good approximation for transition metals and their compounds, we write the Anderson-lattice Hamiltonian in the form

$$H=H_0+\sum_{\mathbf{k}\sigma} t_{\mathbf{k}} c^{+}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}+\sum_{\mathbf{k}m\sigma} (V_{\mathbf{k}lm} c^{+}_{\mathbf{k}\sigma} a_{\mathbf{k}lm\sigma}+\mathrm{H.c.}), \quad (1)$$

where H_0 is the Hamiltonian of intrasite interaction between localized $d(f)$ electrons, $a^{+}_{\mathbf{k}lm\sigma}$ and $c^{+}_{\mathbf{k}\sigma}$ are the creation operators for localized and conduction electrons, respectively; l is the orbital quantum number, t_k is the band energy,

$$V_{\mathbf{k}lm}=\langle \mathbf{k}|V(\mathbf{r})|\mathbf{k}lm\rangle$$

is the matrix element of hybridization. A symmetry analysis of hybridization mixing in various situations is performed in the reviews.[8–10] To simplify the model, we describe the states of conduction electrons by plane waves. Using the expansion in spherical harmonics

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$$\exp(i\mathbf{kr})=4\pi\sum_{lm} i^l j_l(kr)Y_{lm}(\hat{\mathbf{r}})Y^*_{lm}(\hat{\mathbf{k}}), \quad \hat{\mathbf{r}}\equiv(\theta,\varphi), \tag{2}$$

where $j_l(x)$ is the spherical Bessel function, we obtain

$$V_{\mathbf{k}lm}=i^l Y^*_{lm}(\hat{\mathbf{k}})v_l(k), \tag{3}$$

where

$$v_l(k)=4\pi\int_0^\infty r^2 dr R_l(r)v(r)j_l(kr), \tag{4}$$

$R_l(r)$ is the radial wave function, and $v(r)$ is a spherically symmetric potential of the given site.

In the case of jj coupling (actinide compounds) we must replace in (1) lm $\sigma\rightarrow j\mu$, where $j=l\pm 1/2$ is the total electron momentum, and μ is its projection.

In the case of strong interaction H_0 it is convenient to use the representation of the many-electron (ME) Hubbard x operators,[11,12] which reduces H_0 to the diagonal form:

$$H_0=\sum_{iSL\mu M} E_{SL}X_i(SL\mu M,SL\mu M). \tag{5}$$

One-electron operators are expressed in terms of the X operators as follows:

$$\begin{aligned}a^+_{ilm\sigma}=&\sum \sqrt{n}G^{S_nL_n}_{S_{n-1}L_{n-1}}C^{S_n\mu_n}_{S_{n-1}\mu_{n-1},1/2\sigma}C^{L_nM_n}_{L_{n-1}M_{n-1},lm}\\ &\times X_i(S_nL_n\mu_nM_n,S_{n-1}L_{n-1}\mu_{n-1}M_{n-1}),\end{aligned} \tag{6}$$

where C are the Clebsch–Gordan coefficients, and G are the Racah fractional parentage coefficients. The latter quantities satisfy the orthogonality relations

$$\begin{aligned}&\sum_{\{S'L'\alpha'\}} G^{SL\alpha}_{S'L'\alpha'}G^{SL\alpha''}_{S'L'\alpha'}=\delta_{\alpha\alpha''},\\ &n\sum_{SL\alpha}[S][L]G^{SL\alpha}_{S'L'\alpha'}G^{SL\alpha}_{S'L'\alpha''}\\ &\quad=(2[l]+1-n)[S'][L']\delta_{\alpha'\alpha''},\end{aligned} \tag{7}$$

where α are the additional quantum numbers which distinguish different ME terms with the same values of S and L (we omit α for simplicity where possible), and $[A]=2A+1$.

Retaining the two lowest terms for the configurations d^n and d^{n-1}, $\Gamma_n=\{SL\}$, and $\Gamma_{n-1}=\{S'L'\}$ and defining the new electron operators

$$\begin{aligned}d^+_{\mathbf{k}lm\sigma}&=\sum_{\mu\mu'MM'} C^{S\mu}_{S'\mu',1/2\sigma}C^{LM}_{L'M',lm}X_{\mathbf{k}}(SL\mu M,S'L'\mu'M'),\\ c^+_{\mathbf{k}lm\sigma}&=i^lY^*_{lm}(\hat{\mathbf{k}})c^+_{\mathbf{k}\sigma},\end{aligned} \tag{8}$$

we represent the Hamiltonian (1) in the form

$$\begin{aligned}H=H_0+&\sum_{\mathbf{k}lm\sigma}\{t_{\mathbf{k}}c^+_{\mathbf{k}lm\sigma}c_{\mathbf{k}lm\sigma}+\tilde{v}_l(k)\\ &\times(c^+_{\mathbf{k}lm\sigma}d_{\mathbf{k}lm\sigma}+\text{H.c.})\}.\end{aligned} \tag{9}$$

Here

$$\begin{aligned}H_0&=\Delta\sum_{\mathbf{k}lm\sigma} d^+_{\mathbf{k}lm\sigma}d_{\mathbf{k}lm\sigma}+\text{const},\\ \Delta&=E_{SL}-E_{S'L'}-\zeta\end{aligned} \tag{10}$$

(we have passed to the grand canonical ensemble by introducing the chemical potential ξ) and the effective hybridization parameters are given by

$$\tilde{v}_l(k)=\sqrt{n}G^{S_nL_n}_{S_{n-1}L_{n-1}}v_l(k). \tag{11}$$

For rare-earth compounds, where strong spin-orbit coupling should be taken into account in the Russel–Saunders scheme, we may restrict the analysis to two lower multiplets of the $4f$ ion, $\Gamma_n=SLJ$ and $\Gamma_{n-1}=S'L'J'$. Changing in (1) and (6) to the J representation with use of

$$|SLJM_J\rangle=\sum_{\mu M} C^{JM_J}_{S\mu,LM}|S\mu\rangle|LM\rangle \tag{12}$$

and summing the product of the Clebsh–Gordan coefficients with use of a $9j$ symbol

$$\begin{aligned}&\sum_{\mu\mu'MM'} C^{JM_J}_{S\mu,LM}C^{J'M'_J}_{S'\mu',L'M'}C^{LM}_{L'M',lm}C^{S\mu}_{S'\mu',1/2\sigma}\\ &=\sum_{j\mu}\begin{Bmatrix} S & L & J\\ S' & L' & J'\\ 1/2 & l & j\end{Bmatrix}\sqrt{[j][J'][S][L]}C^{j\mu}_{1/2\sigma,lm}\\ &\times C^{JM_J}_{J'M'_J,j\mu}, \quad j=l\pm 1/2,\end{aligned} \tag{13}$$

we derive the Hamiltonian, which is formally similar to the Hamiltonian in the case of jj coupling,

$$\begin{aligned}H=&\sum_{\mathbf{k}j\mu}[\Delta f^+_{\mathbf{k}j\mu}f_{\mathbf{k}j\mu}+t_{\mathbf{k}}c^+_{\mathbf{k}j\mu}c_{\mathbf{k}j\mu}+\tilde{v}_j(k)\\ &\times(c^+_{\mathbf{k}j\mu}f_{\mathbf{k}j\mu}+\text{H.c.})],\\ \Delta=&E_J-E_{J'}-\zeta,\end{aligned} \tag{14}$$

where we have introduced new electron operators

$$\begin{aligned}f^+_{\mathbf{k}j\mu}&=\sum_{M_jM'_j} C^{JM_J}_{J'M',j\mu}X_{\mathbf{k}}(SLJM_J,S'L'J'M'_J),\\ c^+_{\mathbf{k}j\mu}&=i^l\sum_{m\sigma} C^{j\mu}_{1/2\sigma,lm}Y^*_{lm}(\hat{\mathbf{k}})c^+_{\mathbf{k}\sigma},\end{aligned} \tag{15}$$

and the effective hybridization parameters are

$$\tilde{v}_j(k)=(n[j][J'][S][L])^{1/2}G^{SL}_{S'L'}\begin{Bmatrix} S & L & J\\ S' & L' & J'\\ 1/2 & l & j\end{Bmatrix}v_l(k). \tag{16}$$

Thus hybridization effects in ME systems depend strongly on ME quantum numbers S,L,J, and therefore on the atomic number. Such a dependence in the rare-earth element series was discussed in Ref. 13. Experimental study of this correlation, which is similar to de Gennes correlation for the $s-f$ exchange parameter and magnetic ordering temperature, is of great interest. It seems to be promising to trace corresponding ME effects in spectroscopic measurements. Below we discuss the Kondo effect.

3. THE EFFECTIVE $s-d(f)$ EXCHANGE MODEL

In the case where $|\Delta|$ is large in comparison with the width of the $d(f)$ level we may exclude the hybridization term from the Hamiltonians (9) and (14) by a canonical transformation to obtain, respectively,

$$\begin{aligned}H=&-\frac{1}{\Delta}\sum \tilde{v}_l(k)\tilde{v}_l(k')C^{S\mu}_{S'\mu',1/2\sigma}C^{LM}_{L'M',lm}C^{S\mu''}_{S'\mu''',1/2\sigma'}\\&\times C^{LM''}_{L'M''',lm'}[X_{\mathbf{k}-\mathbf{k}'}(SL\mu''M'',SL\mu M)\delta_{\mu'\mu'''}\delta_{M'M'''}\\&+X_{\mathbf{k}-\mathbf{k}'}(S'L'\mu'M',S'L'\mu'''M''')\delta_{\mu\mu''}\delta_{MM''}]\\&\times c^{+}_{\mathbf{k}lm\sigma}c_{\mathbf{k}'l'm'\sigma'},\end{aligned}\tag{17a}$$

$$\begin{aligned}H=&-\frac{1}{\Delta}\sum \tilde{v}_j(k)\tilde{v}_{j'}(k')C^{JM}_{J'M',j\mu}C^{JM''}_{J'M''',j'\mu'}[X_{\mathbf{k}-\mathbf{k}'}\\&\times(JM'',JM)\delta_{M'M'''}+X_{\mathbf{k}-\mathbf{k}'}(J'M',J'M''')\delta_{MM''}]\\&\times c^{+}_{\mathbf{k}j\mu}c_{\mathbf{k}'j'\mu'}.\end{aligned}\tag{17b}$$

For $\Delta<0$ ($\Delta>0$) the filling of the level is n ($n-1$) and only the first (second) term in the square brackets in (17) should be retained.

The Hamiltonians (17) describe the exchange interaction of the conduction electrons with $d(f)$ electrons. It should be noted that in the case under consideration the interaction is strongly anisotropic because of the spherical harmonics which are contained in (8) and (15). This should result in a strong anisotropy of indirect $RKKY$-type $f-f$ interaction, which may be derived in the second order in the $s-f$ exchange. Such an anisotropy is observed in several rare-earth and actinide compounds.

Using the identities of the type

$$\begin{aligned}\sum_{M'} C^{LM}_{L'M',lm}C^{LM''}_{L'M',lm'}=&\sum_{pq}(-1)^{p-q}[p]\sqrt{[L]/[l]}\\&\times\begin{Bmatrix} l & l & p\\ L & L & L'\end{Bmatrix}\\&\times C^{LM''}_{LM,pq}C^{lm}_{lm',p-q},\end{aligned}\tag{18}$$

we can decompose the Hamiltonians (17) into sums of terms corresponding to the interaction of conduction electrons with different multipole components of the orbital and spin (or total momentum) degrees of freedom.

By analogy with the usual $s-d(f)$ exchange model,[1] perturbation theory expansion for the models (17) yields logarithmic corrections to various physical quantities, which indicates reconstruction of the system's state at low temperatures. In particular, such a correction to electron self-energy and resistivity occurs in the third order in the effective $s-f$ exchange parameter, $I\sim v^2/\Delta$. Unfortunately, the complicated tensor structure of the Hamiltonians (17) prevents introducing the unique energy scale for the infrared divergences (the Kondo temperature). However, the calculation of T_{K} may be performed in the case where the energy of the $d(f)$ level Δ does not depend on the ME term and is determined by the number of electrons only (see Appendix I).

4. CALCULATION OF ELECTRON GREEN'S FUNCTIONS. THE KONDO TEMPERATURE

We consider the anticommutator retarded Green's function of localized d electrons in the nonmagnetic phase (the problem of ferromagnetic ordering in the Anderson model with strong correlations was investigated in Ref. 14). The simplest decoupling for the model (1) in the ME representation (6) yields (cf. Ref. 14)

$$\begin{aligned}\langle\langle a_{\mathbf{k}lm\sigma}|a^{+}_{\mathbf{k}lm\sigma}\rangle\rangle_E=\Bigg(\Bigg\{&\sum_{n\{SL\}\{S'L'\}}\frac{n}{2[l]}[S][L]\\&\times(G^{SL}_{S'L'})^2\frac{N_{SL}+N_{S'L'}}{E-E_{SL}+E_{S'L'}}\Bigg\}^{-1}\\&-\frac{|V_{\mathbf{k}lm}|^2}{E-t_{\mathbf{k}}}\Bigg)^{-1},\end{aligned}\tag{19}$$

where the averages

$$N_{SL}=\langle X_i(SL\mu M,SL\mu M)\rangle\tag{20}$$

do not depend on the momentum projections. The corresponding energy spectrum contains a system of subbands, which are separated by hybridization gaps (or pseudogaps) surrounded by density-of-states peaks. In the model with strong correlations (9) we obtain the following expression for the spectrum:

$$E^{1,2}_{\mathbf{k}}=\frac{1}{2}(t_{\mathbf{k}}+\Delta)\pm\left[\frac{1}{4}(t_{\mathbf{k}}-\Delta)^2+\left|\tilde{V}_{\mathbf{k}lm}\right|^2\right]^{1/2},\tag{21}$$

where

$$\tilde{V}_{\mathbf{k}lm}=i^lY_{lm}(\hat{\mathbf{k}})\tilde{v}_l(k)\left\{\frac{[S][L]}{2[l]}(N_{SL}+N_{S'L'})\right\}^{1/2}.\tag{22}$$

We see that the width of the hybridization (pseudo)gap depends appreciably on ME occupation numbers (in particular, on the position of the d level).

The approximation (19) ignores the spin-flip processes, which result in the Kondo effect and can change substantially the structure of the electron spectrum near the Fermi level. The Kondo anomalies can be taken into account by performing a more accurate calculation of the Green's function. For brevity we consider model (14). In model (9) we see that $[J]\rightarrow[S][L]$ and $\tilde{v}_j\rightarrow\tilde{v}_l$.

It is convenient to use the operators, which are averaged over angles of the vector k:

$$f^{+}_{kjm}=\int d\hat{\mathbf{k}}f^{+}_{\mathbf{k}jm},\quad c^{+}_{kjm}=\int d\hat{\mathbf{k}}c^{+}_{\mathbf{k}jm},\tag{23}$$

so that the operators c_{kjm} satisfy the Fermi commutation relations. Following to the consideration of the $SU(N)$ Anderson model in the retarded Green's function method,[15] which uses the idea of the $1/N$ expansion,[9] we write the equation of motion

$$\begin{aligned}(E-\Delta)\langle\langle f_{\mathbf{k}jm}|f^{+}_{\mathbf{k}jm}\rangle\rangle_E=&R_j(1+\tilde{v}_j(k))\langle\langle c_{\mathbf{k}jm}|f^{+}_{\mathbf{k}jm}\rangle\rangle_E)\\ &+\sum_{j'm'\mu M\mathbf{q}}\tilde{v}_{j'}(q)C^{JM}_{J'M,jm}\\ &\times\left\langle\left\langle\left[\sum_{M'}C^{JM}_{J'M',j'm'}X_{\mathbf{k}-\mathbf{q}}\right.\right.\right.\\ &\times(J'M,J'M')\\ &\left.+\sum_{\mu'}C^{J\mu'}_{J'M,j'm'}X_{\mathbf{k}-\mathbf{q}}(J\mu',J\mu)\right]\\ &\times c_{\mathbf{q}j'm'}\left|f^{+}_{kjm}\right\rangle\left.\right\rangle_E,\end{aligned}\tag{24}$$

where we have carried out a decoupling for the term which describes the processes without changing m,

$$R_j=\frac{1}{[j]}\left\{\frac{[J]}{[J']}-\left(\frac{[J]}{[J']}-1\right)\sum_M\langle X(JM,JM)\rangle\right\}.\tag{25}$$

We ignore for simplicity the above-discussed influence of the hybridization gap, which is possible provided that the latter lies far below the Fermi level (note that the corresponding contributions are formally small in the inverse degeneracy of the f level, $1/N$). Carrying out decouplings in the equations for the Green's function on the right-hand side of (24), we obtain

$$\begin{aligned}&(E-t_q)\langle\langle X_{\mathbf{k}-\mathbf{q}}(J\mu',J\mu)c_{\mathbf{q}j'm'}|f^{+}_{kjm}\rangle\rangle_E\\ &\quad=\tilde{v}_{j'}(q)n_q\sum_{M''}C^{J\mu'}_{J'M'',j'm'}\langle\langle X_{\mathbf{k}}(J'M,J\mu'')|f^{+}_{kjm}\rangle\rangle_E,\\ &(E-t_q)\langle\langle X_{\mathbf{k}-\mathbf{q}}(J'M,J'M')c_{\mathbf{q}jm'}|f^{+}_{kjm}\rangle\rangle_E\\ &\quad=-\tilde{v}_{j'}(q)n_q\sum_{\mu''}C^{J\mu''}_{J'M',j'm'}\langle\langle X_{\mathbf{k}}(J'M,J\mu'')|f^{+}_{kjm}\rangle\rangle_E,\end{aligned}\tag{26}$$

where $n_k=\langle c^{+}_{kjm}c_{kjm}\rangle=n(t_k)$ are the Fermi distribution functions. Substituting (26) into (24), averaging over the angles, and using the orthogonality relations for the Clebsh–Gordan coefficients, we find

$$\langle\langle f_{kjm}|f^{+}_{kjm}\rangle\rangle_E=R_j\left[E-\Delta-\sum_f(E)\right]^{-1}\tag{27}$$

$$\sum_f(E)=2\rho\sum_j\tilde{v}^2_j(k_F)\frac{J-J'}{[J']}\ln\left|\frac{D}{E}\right|.\tag{28}$$

Here we have applied the approximation which is usual at considering logarithmic Kondo divergences

$$\sum_{\mathbf{q}}v^2_l(q)\frac{n_{\mathbf{q}}}{E-t_{\mathbf{q}}}\approx\rho u^2_l(k_F)\ln\left|\frac{D}{E}\right|,$$

where D is on the order of the conduction band width, E is referred to the Fermi level, and ρ is the bare density of states of the c electrons at E_{F}.

At $J>J'$ the Green's function (26) has the pole, which is exponentially close to the Fermi level

$$\begin{aligned}|\Delta^*|=T_{\mathrm{K}}\simeq D\exp&\left[-\left(\frac{[J]}{[J']}-1\right)^{-1}\right.\\ &\left.\times|\Delta|\left\{\rho\sum_j\tilde{v}^2_j(k_{\mathrm{F}})\right\}^{-1}\right].\end{aligned}\tag{29}$$

Near this pole we can expand

$$\langle\langle f_{kjm}|f^{+}_{kjm}\rangle\rangle_E\simeq\frac{Z}{E-\Delta^*},\tag{30}$$

where the residue of the Green's function, which determines the inverse effective mass, is

$$\begin{aligned}Z=&R_j\left(1-\frac{\partial\Sigma_f(E)}{\partial E}\right)^{-1}_{E=\Delta^*}\\ \simeq&R_j\frac{2J'+1}{2(J-J')}T_{\mathrm{K}}\left\{\rho\sum_j\tilde{v}^2_j(k_{\mathrm{F}})\right\}^{-1}\ll 1.\end{aligned}\tag{31}$$

Thus the pole (29) determines the characteristic low-energy scale—the Kondo temperature.

5. DISCUSSION

Although derived in a rather complicated way, Eq. (29) has a simple physical meaning: we have in the exponent the ratio of degeneracies of the multiplets Γ_n and Γ_{n-1}.

The usual Kondo effect corresponds to the total compensation of the magnetic moment ($J'=0$). At $J'>J$ the pole (29) is absent (the strong coupling regime does not occur) since the model under consideration is mapped by a canonical transformation into a Coqblin–Schrieffer model with a positive exchange parameter (see Sec. 3).

The result of calculation of the Kondo temperature in the present approximation is valid for the case of a single magnetic impurity. The quantity (29) then determines the position of the Abrikosov–Suhl resonance and, consequently, the characteristic energy and temperature scale for the Kondo anomalies in the thermodynamic and transport properties. The exponential dependence on the external parameters (in particular, on the f-level position Δ) makes it difficult to establish experimentally the reliable correlations of T_{K} with the ME quantum numbers. However, the expression (29) enables us to explain the very low values of T_{K}, which are observed for Tm impurities (these values are not obtained within the large-N approach).[9] In this case the configurations Γ_n and Γ_{n-1} are magnetic: $J=7/2$ for Tm^{2+} and $J=6$ for Tm^{3+}, so that the ratio $(J-J')/(2J'+1)$ in (29) is small.

In a periodic lattice of f moments (anomalous rare-earth and actinide compounds), the Green's function of the conduction electrons has the form

$$\langle\langle c_{kjm}|c^{+}_{kjm}\rangle\rangle_E=[E-t_k-\tilde{v}^2_j(k)\langle\langle f_{kjm}|f^{+}_{kjm}\rangle\rangle_E]^{-1}.\tag{32}$$

As follows from a comparison of (21), (30), and (32), the effective hybridization parameter near E_F is estimated as $v^* \sim (T_{\mathrm{K}}/\rho)^{1/2}$. Thus, instead of the Abrikosov–Suhl resonance, we have a Kondo gap (or pseudogap), which has a width of the order of T_{K}, and corresponding density-of-state peaks occur near the Fermi level. Such a picture of the energy spectrum is characteristic of heavy-fermion compounds.[9,10,16]

For the d impurities [weak spin-orbit coupling, Hamiltonian (9)] an analog of Eq. (29) has the form

$$T_{\mathrm{K}} \simeq D \exp\left(- \left(\frac{[S][L]}{[S'][L']} - 1 \right)^{-1} \frac{|\Delta|}{\rho \bar{v}_l^2(k_{\mathrm{F}})} \right). \tag{33}$$

Note that Eq. (33) satisfies the condition of the particle-hole symmetry ($n \rightarrow n' = 2[1]+1-n$, $\Delta \rightarrow -\Delta$) because of the relation for the fractional parentage coefficients:

$$\{G^{SL}_{S'L'}(n',n'-1)\}^2 = \frac{n[S'][L']}{n'[S][L]} \{G^{S'L'}_{SL}(n,n-1)\}^2. \tag{34}$$

Ignoring the dependence $\Delta(LS)$ we see that all the ME terms of the configurations d^n and d^{n-1} contribute equally to the spin-flip processes, and consequently to the Kondo temperature. The coefficients G which are contained in (11) may then be summed up in the equations of motion with use of the orthogonality relations (7) to obtain

$$n \sum_{\{S''L''\}} \left\{ (G^{S''L''}_{S'L'})^2 \frac{[S''][L'']}{[S'][L']} - (G^{SL}_{S''L''})^2 \right\} = 2[l]+1-2n. \tag{35}$$

For the Kondo temperature we find

$$T_{\mathrm{K}} \simeq D \exp\left(- \frac{1}{2[l]+1-2n} \frac{1}{|I|\rho} \right), \quad I = \frac{v_l^2(k_{\mathrm{F}})}{\Delta}. \tag{36}$$

Note that expression (36) may be represented in the following form, which is similar to (33):

$$T_{\mathrm{K}} \simeq D \exp\left(- \left(\frac{2[l]+1-n}{n} - 1 \right)^{-1} \frac{1}{n|I|\rho} \right). \tag{37}$$

Here the factor $(2[l]+1-n)/n$ is the ratio of the statistical weights for the configurations d^n and d^{n-1}:

$$\frac{2[l]+1-n}{n} = \frac{(2[l])!}{n!(2[l]-n)!} \left[\frac{2[l]!}{(n-1)!(2[l]-n+1)!} \right]^{-1}.$$

The experimental dependence of the Kondo temperature of the transition-metal impurities in copper and gold[4] on the d-electron number demonstrates a sharp minimum in the middle of the series ($n=5$). In the review[4] these data were interpreted on the basis of the Schrieffer model[5] with the Hamiltonian

$$H_{sd} = -\frac{I}{n} \sum_{\mathbf{kk}'\sigma\sigma'} S\sigma_{\sigma\sigma'} \sum_m c^{+}_{\mathbf{k}m\sigma} c_{\mathbf{k}'m\sigma'}, \tag{38}$$

which is rather artificial (see the Introduction). This model yields the n dependence of T_{K}, which is different from (36),

$$T_{\mathrm{K}} \simeq D \exp\left(- \frac{n}{2|I|\rho} \right). \tag{39}$$

The Kondo temperature was calculated by Hirst,[6] without allowance for the intraconfiguration splittings, from the second Born high-temperature estimate for the resistivity in the $s-d$ exchange model. If the coupling parameter is constant in the $3d$ series, the value of T_{K} turns out to be independent of n. We believe that this result is erroneous, since our calculations for the same model within essentially the same approximations (see Appendix I) yield the result (A6), which differs from (36) by unity in the denominator of the exponential function only. Such a difference is typical for the calculation of the Kondo temperature in the degenerate Anderson model[9,15] and is explained by the fact that this approach is justified, strictly speaking, only in the limit of large N. Thus, our results, obtained for the ground state of the degenerate Anderson model, agree with the results of high-temperature perturbation theory in the $s-d$ exchange model.

The fit of the Kondo temperature to the experimental data[4] according to (A6), which corresponds to $|I|\rho = 1/16$, is shown in Fig. 1. Note that the fit to the Schrieffer formula (38) yields the unreasonably large value $|I|\rho = 1/4$.

The LS and crystal-field splittings were introduced in Ref. 6 to improve the agreement with the experimental data. The method of irreducible tensor operators did not allow us to take into account the splittings in the energy denominators which correspond to the Schrieffer–Wolff transformation from the Anderson model to the $s-d$ exchange model. In contrast with Ref. 6, we have calculated the Kondo temperature on the basis of the Anderson model which describes the low-energy (low-temperature) behavior. This model allows us to take into account the dependence of the energy levels on the ME term quantum numbers. This dependence seems to be important, since the distance between different terms in the free atoms is on the order of several electron volts. Because of the separation of the lowest terms for the configurations d^n and d^{n-1}, the results of our calculations, in contrast with those of Ref. 6, include the fractional parentage coefficients. However, direct use of Eq. (33), which yields a strongly oscillating dependence $T_{\mathrm{K}}(n)$, in contradiction of the experimental data, probably overestimates the role of many-electron term effects.

Although the general picture of ion levels (especially in a crystal field) is very complicated, from a general point of view the presence of the factors $(G^{SL}_{S'L'})^2$ is expected to lead to a further strengthening of the dependence $T_K(n)$. The n dependence of the fractional parentage coefficients on the average has a minimum in the middle of the d series. Such a dependence, which is due to the total number of ME terms, is maximum near $n=5$ for combinatorial reasons, and for a given n the values of G^2 satisfy the sum rules (7).

We have restricted the discussion to the case of LS splitting and ignored the crystal-field effects which are very important for the d ions and f ions like Ce^{3+}. In particular, CF results in that $L=0$ for some d impurities (e.g., for V and Ni). The CF splitting may be taken into account by performing more cumbersome calculations with use of the Clebsh–Gordan and fractional parentage coefficients for a point group (see, e.g., Ref. 17). It can be assumed that such calculations should improve the corresponding results of Ref. 6

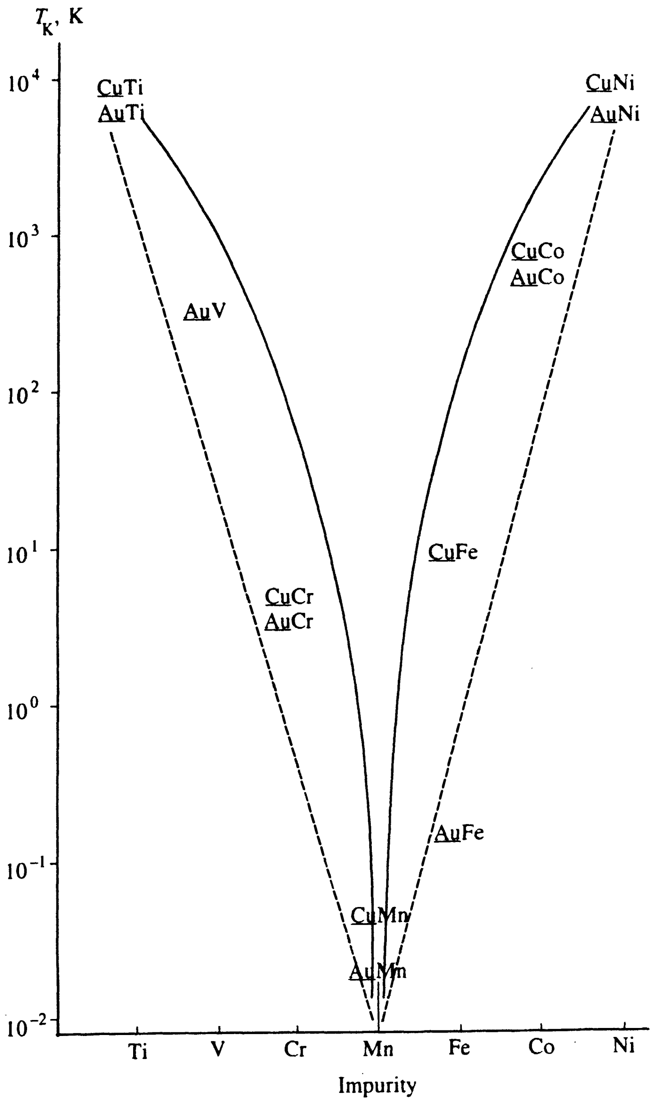

FIG. 1. Experimental data for the d impurities in copper and gold[4] and theoretical curves (A6) (solid line) and (39) (dashed line). The $s-d$ exchange parameter is assumed to be independent of n.

which seem to use, as discussed above, the incorrect zero-order approximation. For accurate estimates of T_K the influence of several groups of degenerate levels (e.g., those corresponding to different atomic or crystal-field split terms) should be taken into account (see Ref. 9). However, these detailed studies require additional information on the electronic structure of Kondo impurities.

The role of variation of the interconfiguration splitting should be also discussed. It was assumed in the estimates of Refs. 5 and 6 that the effective $s-d$ parameters, i.e., the values of v, Δ, and ρ do not depend on the configuration d^n. It is well known, however, that in the many-electron picture these configurations have different stabilities (e.g., the value of Δ should be related to the atomic ionization potentials). In particular, the stability of the spherically symmetric configuration d^5 may result in a large value of $|\Delta|$, which lowers the T_K for manganese.

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APPENDIX I

Consider the calculation of the Kondo temperature for the localized degenerate d level with the configuration d^n $(n\leqslant 5)$, without allowance for the intraconfiguration splitting. The dependence on the quantum numbers of the ME terms will then vanish. The Hamiltonian of the one-impurity $s-d$ exchange model therefore takes the form (cf. Ref. 6)

$$H=\sum_{\mathbf{k}m} t_{\mathbf{k}} c^{+}_{\mathbf{k}m} c_{\mathbf{k}m}$$

$$-I\sum \Big[X(\{m_1\ldots m_{n-1},m'\},\{m_1\ldots m_{n-1},m\})$$

$$-\frac{1}{2[l]}\,\delta_{mm'}\Big] c^{+}_{\mathbf{k}m} c_{\mathbf{k}'m'}, \tag{A1}$$

where all the indices in the sets $\{m_i\}$ $(m_i=1,2\ldots 2[1]=10$ include the spin and orbital projections) are different; the second term in the brackets is subtracted to exclude the potential scattering, $I<0$. The Kondo temperature is determined from the pole of the T matrix which is defined by

$$\langle\langle c_{\mathbf{k}m}|c^{+}_{\mathbf{k}'m}\rangle\rangle_E=\frac{\delta_{\mathbf{k}\mathbf{k}'}}{E-t_{\mathbf{k}}}+\frac{T_{\mathbf{k}\mathbf{k}'}(E)}{(E-t_{\mathbf{k}})(E-t_{\mathbf{k}'})}. \tag{A2}$$

We write the equation of motion

$$(E-t_{\mathbf{k}'})\langle\langle c_{\mathbf{k}'m}|c^{+}_{\mathbf{k}m}\rangle\rangle_E=\delta_{\mathbf{k}\mathbf{k}'}-I\sum_{\mathbf{p}} \Gamma_{\mathbf{kp}m}(E), \tag{A3}$$

$$\Gamma_{\mathbf{kq}m}(E)=\sum_{m_1\ldots m_{n-1},m'}\left\langle\left\langle\Big[X\Big(\{m_1\ldots m_{n-1},m'\},\{m_i,\ldots,\right.\right.$$

$$\left.\left.\times m_{n-1},m\}-\frac{\delta_{mm'}}{2[l]}\Big]c_{\mathbf{q}m'}\right|c^{+}_{\mathbf{k}m}\right\rangle\right\rangle. \tag{A4}$$

To obtain the Kondo terms in the equation of motion for the Green's function (A4), we calculate after some combinatorics the commutator of the operator $X(\{m_i,m'\},\{m_i,m\})$ with the Hamiltonian. Performing an analog of the Nagaoka decoupling (see Ref. 1), we derive

$$(E-t_{\mathbf{q}})\Gamma_{\mathbf{kq}m}(E)=-I\Big\{1-[l]^{-1}(2[l]-n+1)^{-1}+\frac{1}{4}[l]^{-2}$$

$$+(n-2)\sum_{m'm''\mathbf{p}}\Big\langle c^{+}_{\mathbf{p}m''}c_{\mathbf{q}m'}\Big[X(\{m_1,\ldots,$$

$$\times m_{n-1},m'\},\{m_1,\ldots,m_{n-1},m''\})$$

$$-\frac{1}{2[l]}\,\delta_{m'm''}\Big]\Big\rangle\Big\}\sum_{\mathbf{k}'}\langle\langle c_{\mathbf{k}'m}|c^{+}_{\mathbf{k}m}\rangle\rangle_E$$

$$-I\Big[(2[l]-2n+2)n_{\mathbf{q}}-n-1$$

$$-\frac{1}{2[l]}\Big]\sum_{\mathbf{p}}\Gamma_{\mathbf{kp}m}(E). \tag{A5}$$

Solving Eq. (A5), we obtain the estimate for T_{K} from the divergence in the "parquet" approximation (which corresponds to the second Born approximation for resistivity)

$$T_K \simeq D \exp\left(- \frac{1}{2[l]-2n+2} \frac{1}{|I|\rho} \right). \tag{A6}$$

For the second half of the d series $n>5$ the degeneracy of the configuration d^n is smaller than that of d^{n-1}. We must therefore consider the case in which the level d^n lies above the Fermi level; i.e., $\Delta>0$ (otherwise, the Kondo effect is absent). We may then transform to the hole representation and reproduce the result (A6) with the replacement $n \rightarrow 2[l]-n$.

[1] J. Kondo, in *Solid State Physics*, Vol. 23, eds. F. Seitz and D. Turnbull, New York, Academic Press, 1969, p. 183.

[2] K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975); P. W. Anderson, J. Phys. C **3**, 2346 (1970); P. Nozieres and A. Blandin, J. Phys. (Paris) **41**, 193 (1980).

[3] A. M. Tsvelick and P. B. Wiegmann, Adv. Phys. **32**, 745 (1983). N. Andrei, K. Furuya, and J. H. Loewenstein, Rev. Mod. Phys. **55**, 331 (1983).

[4] M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. **40**, 380 (1968); J. Appl. Phys. **40**, 1056 (1969).

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

[6] L. L. Hirst, Z. Phys. **244**, 230 (1971); Int. J. Magn. **2**, 213 (1972).

[7] L. L. Hirst, Adv. Phys. **21**, 295 (1972).

[8] L. L. Hirst, Adv. Phys. **27**, 231 (1978).

[9] D. M. Newns and N. Read, Adv. Phys. **36**, 799 (1987).

[10] P. Fulde, J. Keller, and G. Zwicknagl, *Solid State Physics*, Vol. 41, eds. F. Seitz *et al.*, New York, Academic Press, 1988, p. 1.

[11] J. Hubbard, Proc. Roy. Soc. A **285**, 542 (1965).

[12] V. Yu. Irkhin and Yu. P. Irkhin, Fiz. Metallov Metalloved. **76**, No. 6, 49 (1993) [Phys. Metals Metallography **76**, 578 (1993)]; Phys. stat. sol. (b) **183**, 9 (1994).

[13] Yu. P. Irkhin, Fiz. Tverd. Tela **30**, 1202 (1988) [Sov. Phys. Solid State **30**, 697 (1988)].

[14] K. A. Kikoin and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **58**, 2184 (1970) [Sov. Phys. JETP **31**, 1179 (1970)].

[15] V. Yu. Irkhin and M. I. Katsnelson, Z. Phys. B **75**, 67 (1989).

[16] F. Marabelly and P. Wachter, J. Magn. Magn. Mat. **70**, 364 (1989).

[17] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge, University Press, 1961; *The Irreducible Tensor Method for Molecular Symmetry Groups*, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.

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